Master's Thesis

Study of absorption process for carbon dioxide / methane separation based on pressure swing

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(Environmental Science and Engineering)

Graduate School of UNIST

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Abstract

Currently, global warming is accelerating and greenhouse gases are known to be the main cause. Therefore, various studies on the reduction of greenhouse gases have been carried out in order to solve global warming around the world. The purpose of this study is to separate carbon dioxide and methane from biogas in anaerobic digesters to reduce carbon dioxide, which accounts for a large proportion of greenhouse gases.

As a criterion for selecting a suitable solvent, not only the reduction of carbon dioxide but also the recycling of collected carbon dioxide was also observed. This study on the solvent which plays a dominant role in the physical interaction rather than the chemical interaction with the carbon dioxide enables us to improve the reuse efficiency of the solvent through the increase and decrease of the pressure.

In order to find a suitable solvent for the purpose of the experiment, the solvent was divided into five categories. Water was used as a basic comparison of the experiments and pure solvents were used to increase the dissolved amount of carbon dioxide. We also used an aqueous solution of artificial seawater with salt added to the water to determine how salt influences the degassing of the anaerobic digestion gas (AD gas). The aqueous solution was used to confirm the synergy effect between water and solvent. Finally, the experiment was carried out by mixing acetone-based solutions with various advantages in pure solvent form.

To maximize the merits of each solvent, we have combined three tertiary systems: water with the advantage of increasing the rate of carbon dioxide degassing, salt that can lead to a salting out effect, and acetone, which can increase the solubility of carbon dioxide. Compared with other experimental conditions in the tertiary system, it was possible to capture a high rate of carbon dioxide in the degassed AD gas with increasing solubility of carbon dioxide. It is concluded that the tertiary system is the best condition for the experimental purpose in the case of containing a small amount of water.

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Chapter 1. Introduction

Global warming is considered to be one of the most serious environmental problems in the world. [1] Global warming raises sea level due to glacier melting and causes problems such as rising surface temperatures of the earth, expansion of the subtropical desert, changes in precipitation patterns, and extreme climates such as heat and extreme weather in summer and winter. [2] The reason for global warming has not been clarified, but the main cause is thought to be caused by human beings, such as increasing greenhouse gas concentrations and the use of fossil fuels. [3] From the beginning of the 21th century until 1980, the average temperature of the earth rose by 0.8℃. The temperature rise in this trend is rapidly increasing every year, and international efforts are being made to prevent global warming by preventing global warming. [4]

GHG refers to a gas that serves to raise the temperature of the Earth's surface. Gases, which are coupled by two or more different atoms, correspond to greenhouse gases. It is known that greenhouse gases absorb or reflect infrared radiation emitted from the earth's surface to space and raise the temperature. [5] Representative greenhouse gases on Earth include water vapor, carbon dioxide, nitrous oxide, methane, and ozone. [5] Due to natural greenhouse gas emissions, the temperature rise of about 33℃ is maintained and the current average surface temperature of 15℃ is maintained. However, if these gases are present in excess of the proper amount, the energy absorbed and released by the greenhouse gases becomes excessive, and the average temperature of the earth rises above the appropriate temperature due to the natural greenhouse effect. This effect is called the enhanced greenhouse effect, which results in global warming, where the temperature of the Earth rises above average. [6]

The contribution of the greenhouse effect by gases is determined by the amount and nature of the presence of each gas. For example, methane is a greenhouse gas that is stronger than carbon dioxide but has less impact on the greenhouse effect because the concentration in the atmosphere is lower than that of carbon dioxide. The global warming potential (GWP) has a value of 21 for methane, 310 for nitrous oxide, and 23900 for sulfur hexafluoride when the warming index of carbon dioxide is taken as 1. [7]

After industrialization, the concentration of carbon dioxide showed a large increase. In addition to the naturally occurring carbon dioxide, greenhouse gases that are artificially created by humans cause great problems. Naturally occurring carbon dioxide can maintain its equilibrium by self-limiting action, but anthropogenic carbon dioxide is released indiscriminately and accumulates in the atmosphere, causing problems. [8] Greenhouse gases arise from the burning of fossil fuels, deforestation and the fermentation of bacteria in the manure of livestock due to the large number of livestock breeding. [9] Carbon dioxide in the greenhouse gases is mainly generated by industrial processes and energy use, and methane is mainly generated in waste, agriculture, and livestock. The concentration of carbon dioxide

in the atmosphere has increased from the excessive use of fossil fuels. Methane is more abundant than artificially generated, mostly from waste sources such as wetlands and landfills, and biomass burning. [10]

The major source of carbon dioxide and methane gas is biogas. [11] Biogas is a mixture of gases in which organic matter is decomposed and produced under oxygen-free conditions. Biogas is produced from sewage, food waste, and manure, and is considered a renewable energy source. [12] Biogas is generated by anaerobic digestion by anaerobic organisms, and methane and carbon dioxide are the main constituents. The mechanism of generation of biogas is as follows. [13]

$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$

Although biogas varies slightly depending on the source, methane has a composition of 50 to 75%, Carbon dioxide has a composition of 25 to 50%, and nitrogen, hydrogen sulfide, and other gases are present in small amounts. [14] By separating methane and carbon dioxide, methane can be used as a fuel for heating energy sources. Carbon dioxide is trapped in the air without releasing it, enabling conversion to other energy through catalysis. [15]

Seawater accounts for 97.2% of the total water on Earth. In fact, the amount of water that we can use is small, so research is underway to use seawater through seawater desalination to solve this problem. [16] Experiments were carried out in artificial seawater conditions to determine the possibility of using seawater in an unlimited amount of seawater for the capture of carbon dioxide without further purification of seawater. If seawater can be used in carbon dioxide absorption processes, the amount of water that can be used on the earth can be increased, and at the same time, environmental effects can be expected.

Acetone has the advantage of mixing well with most solvents such as water, alcohols, and ethers. [17] Acetone can also be easily obtained through a variety of processes. Acetone plays a very important role as a solvent, and is widely used for the production of plastics, the dissolution and storage of acetylene, and the raw materials for organic synthesis. It is also known as an organic substance with high solubility in carbon dioxide. [18] We have investigated the possibility of utilizing the structural characteristics of acetone, which is commonly used in everyday life, in the capture of carbon dioxide.

Chapter 2. Background

There are three main types of research for reducing carbon dioxide. Absorption, separation membrane, and adsorption method are mainly studied. [19] There are two main types of absorbents in the absorption technology used for carbon dioxide capture. [20] Carbon dioxide may be separated through chemical reaction or by physical reaction. Fig. 1 shows the classification of the absorbents used for carbon dioxide capture.

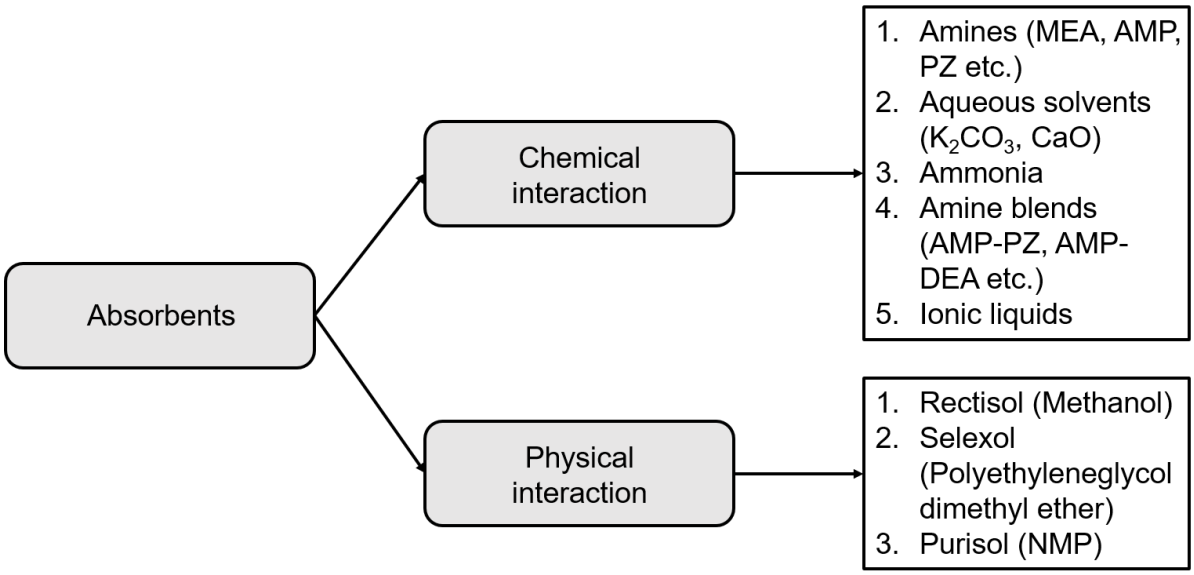


Fig. 1 Classification of absorbents used in absorption technology of carbon dioxide capture

2.1 Absorption method

Fig. 2 describes a schematic diagram of an absorption method for absorbing gas into a solvent. The gas and the liquid come into contact in a countercurrent flow in the absorber and the gas is dissolved in the liquid.

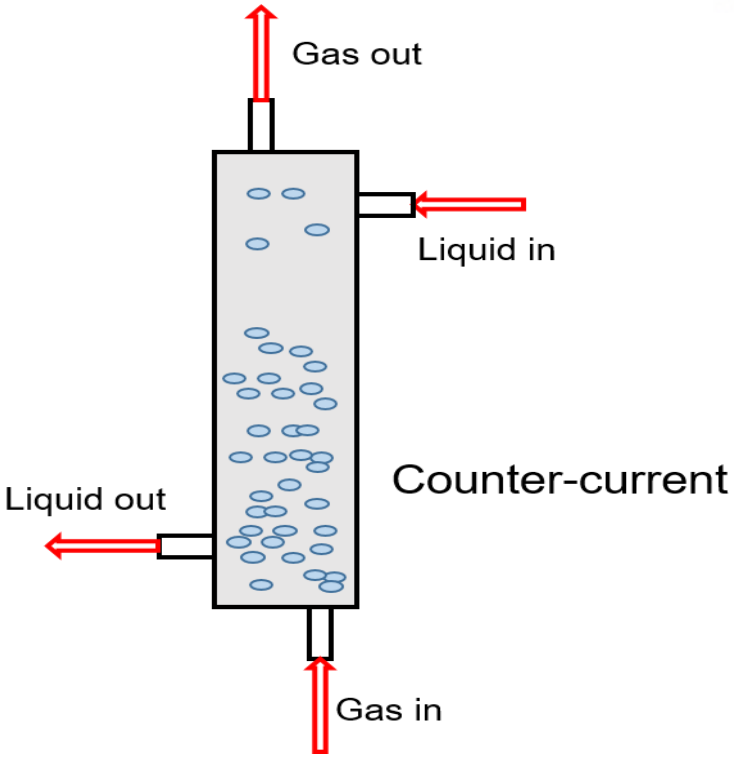


Fig. 2 Gas absorption process schematic diagram [21]

Chemical reacting absorbents include amines, aqueous solvents, ammonia, and ionic liquids. [22] Chemical reacting substances have great advantages in terms of the removal of carbon dioxide. Blends are used to combine the advantages of different absorbents to offset the drawbacks. Physical absorbents include Rectisol, Selexol, and Purisol. The materials used for physical absorbents are used in consideration of high reactivity, carbon dioxide absorption capacity, low vapor pressure, easy regeneration method, and economical aspects. [23, 24] The techniques used in the absorption process are described below.

2.1.1 Water scrubbing

Water scrubbing is a method of absorbing gas using water as a solvent. [25] The gas moves to the absorber and the gas is absorbed into the water at high pressure. Gas such as biogas, which is the gas to be treated, is compressed to 6-10 bars through the compressor and injected into the lower part of the absorption tower. In general, the interior of the tower is filled with a filler to widen the contact area between the gas and the liquid. Water and biogas are contacted in counter-current flow to maximize carbon dioxide removal rate and reduce energy consumption and methane loss. During this process, carbon dioxide and trace amounts of methane are physically absorbed in water (solvent). The high efficiency of this process arises from the property that Henry's constant for carbon dioxide in water is

about 25 times higher than methane. [26] Decreasing the water temperature increases the absorption of carbon dioxide, while lowering the operating pressure reduces the water flow. However, the flow of water depends on the flow of the total gas flowing through the absorber, so the pressure and temperature depend on the solubility constant of carbon dioxide. [27] After the absorption, the used water moves to the desorption column and blows air at atmospheric pressure to release the dissolved carbon dioxide.

2.1.2 Amine absorption / scrubbing

It is the most widely used technique among absorption methods using liquid media. [28] This process uses amines for acid gases such as carbon dioxide and hydrogen sulphide. The acidic gas, carbon dioxide, is selectively absorbed into the aqueous base solution in ambient conditions. The solvent is then regenerated through heating of the solution at a temperature near 100°C and a significant amount of energy is required in the process. [29] A high energy requirement for regeneration is a major drawback to this method. The use of ionic liquids, a recently used environmentally friendly substance, has great potential for the absorption of carbon dioxide. [30] The mechanisms of amine and carbon dioxide are as follows.

2.1.3 Organic solvent sorption / scrubbing

The most common combination of organic solvents for carbon dioxide absorption is a mixture of dimethyl ether and Poly Ethylene Glycol. [31] The principle of this method is based on a physical scrubbing process like a water scrubbing method. The organic solvent has a carbon dioxide solubility that is 5 times higher than that of water. [32] In addition, the organic solvent mixture is characterized by low freezing point, and this feature can be advantageous in that the system can be operated at temperatures below -20°C without additional heat supply. However, the organic mixture has corrosiveness, which causes corrosion of the equipment. [33]

2.2 Membrane separation method

A separation membrane is defined as a boundary layer capable of selectively separating a specific component from a mixture of two or more components. [34] The separation using a separation membrane can be determined not only by the difference in particle size, but also by the difference in concentration, the charge repelling force, the difference in solubility of a specific component with respect to the material of the separation membrane. For the gas separation membrane, a porous membrane and a nonporous membrane are used. [35] If the gas mixture is diffused from the high

pressure to the low pressure through the porous membrane at a pressure difference, the gas having a small molecular weight has a faster diffusion rate and can pass through the membrane well. Due to the difference in molecular weight, the gas permeates at different rates depending on the type of gas. Fig. 3 describes the order of permeation rate of gas. [36]

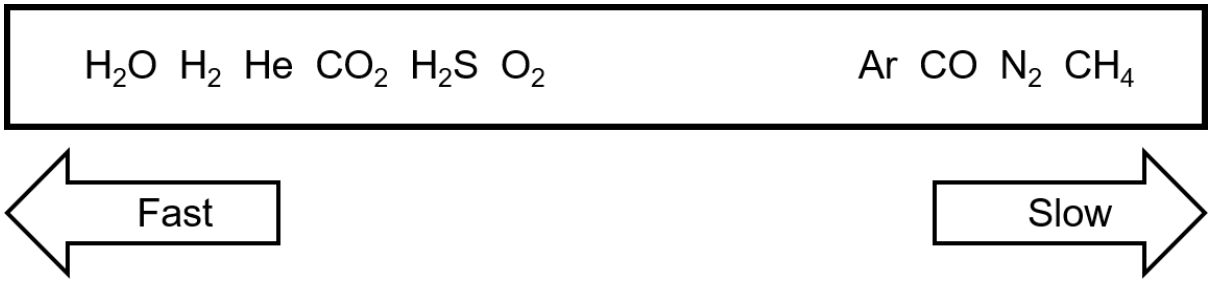


Fig. 3 Order of permeation rate of gas

The gas permeation mechanism by the nonporous membrane has a mechanism different from that of the porous membrane. As a non-porous membrane, a polymer membrane is generally used, and the gas separation occurs due to the difference between the molecules dissolved and diffused into the polymer membrane. [37] The mechanisms of gas permeation are divided into three stages. Gas is absorbed or adsorbed on the surface of the raw material mixture gas side separation membrane and is desorbed to the permeation side through diffusion through the polymer membrane. [38] This principle is expressed in a schematic diagram as Fig. 4.

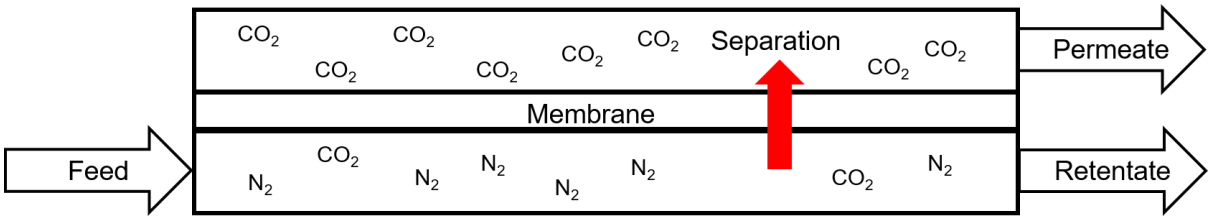


Fig. 4 Principle of gas separation membrane

When applying a dense membrane for separation, the membrane acts as a very specific filter. Membranes used for the separation of Biogas hold methane while permeating the carbon dioxide through the membrane. Contaminants such as water vapor and nitrogen contained in the raw biogas are removed during the separation process. Various factors and mechanisms control the performance and efficiency of membrane-based carbon dioxide removal technology. In addition, the morphology of membrane materials plays an important role for interaction with other gas molecules. [39] The membrane process has the advantage that no chemical or solvents are required and that the process can

be rescaled without significant efficiency loss. The process of the gas separation membrane is as Fig. 5.

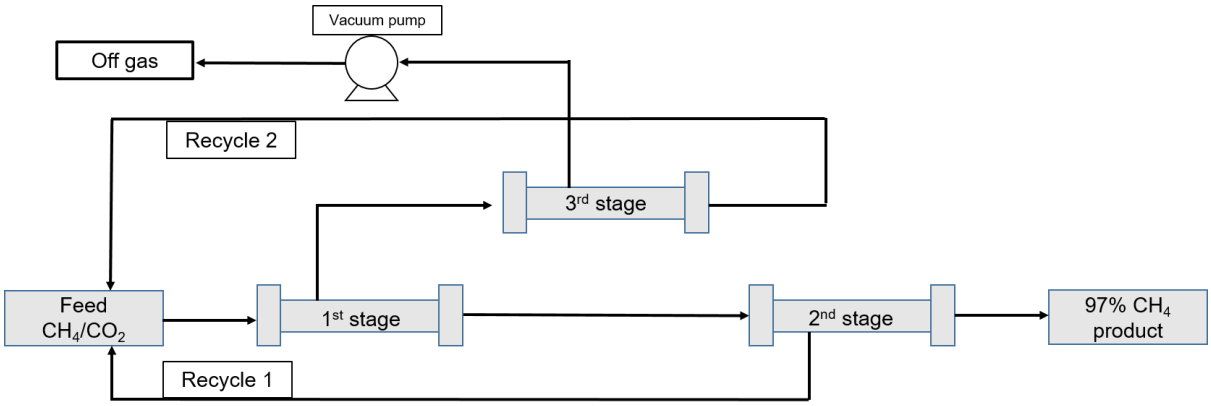


Fig. 5 Schematic diagram of gas separation process

2.3 Adsorption method

Adsorption technology using solid adsorbents for carbon dioxide capture is one of the best technologies for CCS. [40] Gas adsorption is the process of separating gas components from a gas stream using solid materials. The gas component is in contact with the solid and is adsorbed on the solid surface in the gas phase. There are several considerations in adsorption for carbon dioxide capture. High carbon dioxide adsorption capacity, large surface area of adsorbent, fast kinetics of adsorption reaction, high selectivity for carbon dioxide, mild sorbent regeneration conditions, stability during adsorption / desorption cycle, low cost of adsorbent should be considered. [41]

The adsorption process requires a pretreatment process to reduce the concentration of impurities such as nitrogen oxides, sulfur oxides, and water vapor present in the gas during the carbon dioxide adsorption process of the flue gas stream. [42] This impurity may occupy the adsorption site, which may reduce the space to be adsorbed by the carbon dioxide molecule, and the adsorption amount of the carbon dioxide may be reduced in this process. It is especially important to dry the flue gas before the adsorption. Water can take up adsorption sites as well as cause damage to the crystal structure of some adsorbents. After pretreatment for impurities, the gas should be cooled to room temperature. Most adsorbents are due to the rapid decrease in adsorption capacity at high temperatures. Depending on the type of adsorbent, strong chemical interactions may occur with weaker physical interactions. Physical adsorption is usually caused by lower reaction heat than chemical adsorption and reduces the energy consumption of the desorption stage. [43] After adsorption, solid adsorbents migrate to desorption stage. During the desorption, the gaseous carbon dioxide adsorbed is released from the adsorbent, and the adsorbent is reused through the regeneration process. Fig. 6 is a schematic diagram showing the gas

adsorption process. [44]

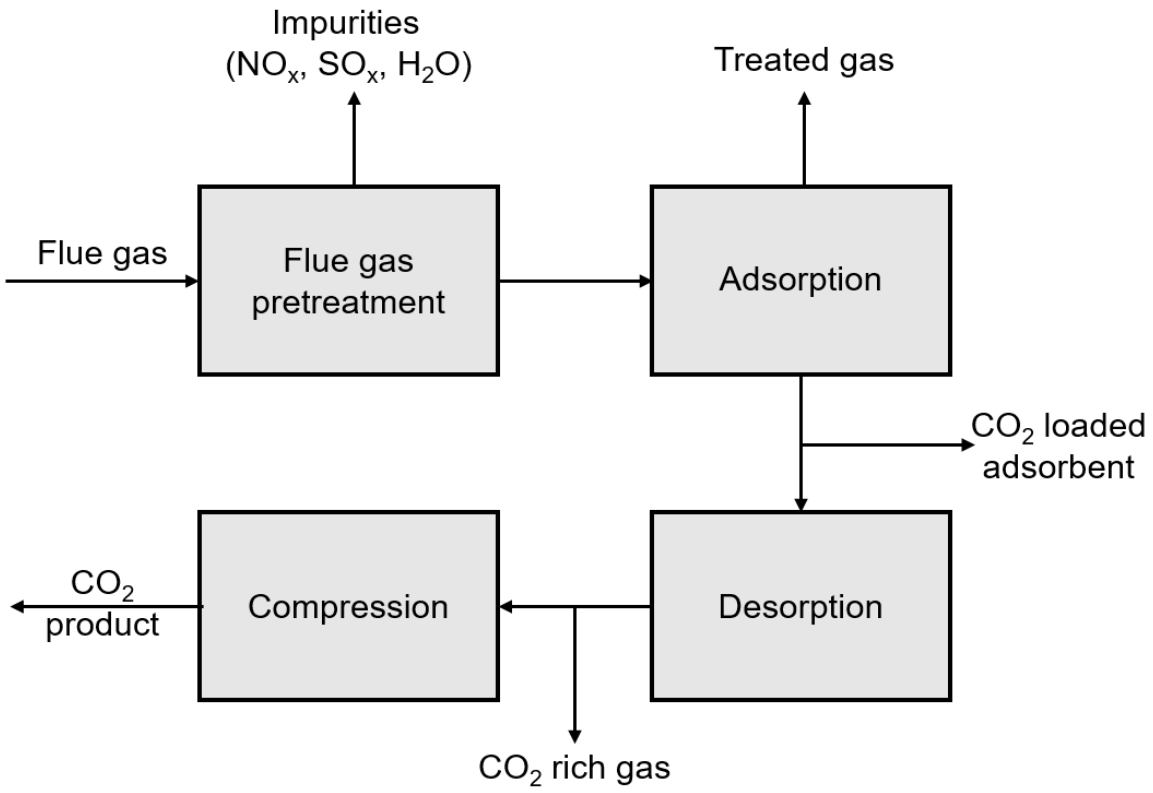


Fig. 6 Gas adsorption process schematic diagram

In the desorption process, pressure swing and temperature swing methods are widely used. [45] In the pressure swing system, the adsorption stage is carried out with increasing pressure and when the pressure of the system is reduced, carbon dioxide is desorbed from the adsorbent. In a temperature swing system, the temperature of the system increases as carbon dioxide is adsorbed from the adsorbent. The advantage of the temperature swing system is that it maintains a high carbon dioxide partial pressure and can regenerate the adsorbent. This advantage avoids high energy requirements during recompression of carbon dioxide. However, the regeneration of the pressure swing system takes a short time, but the temperature swing system requires a long regeneration time. Adsorbents are mainly used for zeolites, activated carbon, amine functionalized adsorbents, and metal organic frameworks (MOFs). [46] The advantages and disadvantages of each adsorbent are summarized in the Table. 1. [15]

Table. 1 Advantages and disadvantages of Adsorbents for adsorption

	Advantages	Disadvantages
Zeolites	1. Favorable adsorption kinetics 2. High adsorption capacity at mild operating conditions (0-100℃, 0.1-1 bar carbon dioxide) 3. Suitable for carbon dioxide capture from post combustion gas streams	1. Presence of impurities impact performance 2. For complete regeneration, desorption must occur the energy and time due to chemisorb
Activated carbon	1. High thermal stability 2. Favorable adsorption kinetics 3. Lower raw material costs 4. Large adsorption capacity at elevated pressures 5. Desorption can easily be accomplished by the PSA	1. Low carbon dioxide capacity at mild conditions 2. Negatively impacted by NOx, SOx and H_2O
Amine functionalized adsorbents	1. Adsorption capacity Minimally impacted by carbon dioxide partial pressure 2. Humid environments improve adsorption efficiency 3. Favorable adsorption kinetics	1. Degrade at temperatures around 100℃ 2. Irreversible reactions with NOx and SOx produce unwanted byproducts 3. A TSA is needed for desorption
Metal organic frameworks (MOFs)	1. High thermal stability 2. Adjustable chemical functionality 3. Extra high porosity 4. High adsorption capacity at elevated pressures (35 bar carbon dioxide) 5. Easily tunable pore characteristics	1. Negatively impacted by NOx, SOx and H_2O 2. Low carbon dioxide selectivity in carbon dioxide/nitrogen gas streams 3. PSA, TSA have not been adequately researched

The characteristics of the adsorption, separation membrane and adsorption method used for gas separation have been summarized so far. The advantages and disadvantages of absorption, separation membrane and adsorption method are summarized Table. 2. [19] Finally, we describe the directions to be studied for each method in Table. 3. [47]

Table. 2 Advantages and disadvantages of absorption, separation membrane, adsorption method

	Advantages	Disadvantages
Absorption	1. Re-use of carbon dioxide possible 2. No pre-treatment necessary 3. Proven technology	1. Disposal waste water 2. Use of process water
Membrane	1. Dry process 2. No chemicals 3. Compact process	1. Pre-treatment necessary 2. High investment costs 3. Unstable long-term 4. Low methane recovery
Adsorption	1. Dry process 2. No use of chemicals 3. High gas quality	1. H_2S pre-treatment 2. Complex process 3. High investment cost

Table. 3 Carbon dioxide capture technologies and its future directions [48]

	Critical issue for large scale application	Future needs / emerging trends
Absorption	Energy requirement for regeneration	Solvents with high carbon dioxide capacity and low regeneration energy
Membrane	Carbon dioxide selectivity Degradation / fouling issue	Enhanced permeability and selectivity
Adsorption	Low capacity / selectivity Long cycle times	Adsorb carbon dioxide in presence of water vapor

2.4 Objective of this research

In this study, experiment to separate carbon dioxide and methane from biogas, a major source of greenhouse gases, was conducted using a solvent absorption method. Studies that have been conducted so far have focused on the removal of carbon dioxide gas. In previous studies, data on the selectivity of carbon dioxide and methane and the aspects of gas degassed from the solution have not been studied. In this work, we considered the recycling aspect of removed carbon dioxide. In order to recover high purity methane by removing carbon dioxide from raw material gas through continuous process and to degassed absorbed carbon dioxide and recycle it, this study was conducted to find a solvent capable of degassing carbon dioxide only by physical method. Vacuum purging, stirring, and pressure increase / decrease were used for the regeneration process, and this study was conducted to find a solvent that maintains efficiency after regeneration through physical methods. The salting out effect is a purification method that reduces the solubility of specific molecules in solutions with very high ionic strength. [49] The solubility of ions that can be dissolved in a solution depends on the ionic strength of the solution. When an excess of salt is added to the solution, the amount of ions that can be dissolved decreases with increasing ionic strength. By using these effects, we tried to capture the excessive amount of dissolved carbon dioxide through abrupt change of pressure. Through the pressure swing method, which increases or decreases the pressure of the pressurized solution, the possibility of recycling of carbon dioxide in the gas being degassed from the solution was studied. Solvents which are chemically bonded require high temperature heating during regeneration process and also cause a lot of solvent loss in this process. We focused on the advantage of minimizing energy through regeneration of physical methods. To achieve this purpose, we focused on solvents that physically interact with carbon dioxide.

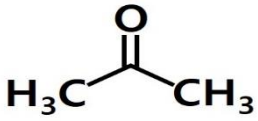
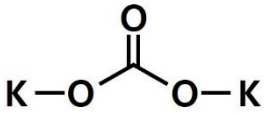
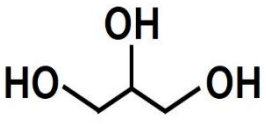
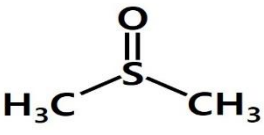
Chapter 3. Materials and methods

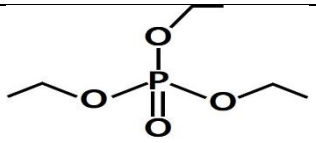
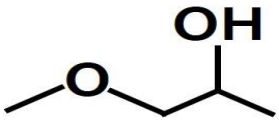
3.1 Materials

This study was carried out by dividing the types of solvents used for carbon dioxide absorption process into five categories: water, aqueous solution, pure solvent, salt containing artificial seawater, and acetone base solution.

The type and structure of the solvent used in the aqueous solution are shown in the Table. 4. The solvent used in the aqueous solution was MEA, K_2CO_3, which had strong base properties, and an organic solvent having various functional groups.

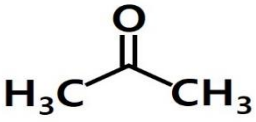
Table. 4 Structure and physical properties of solvent used in aqueous solution experiment

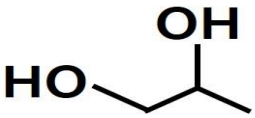
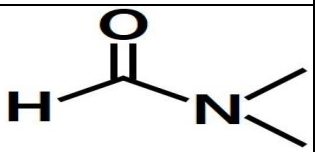
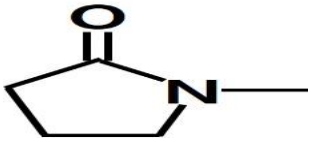
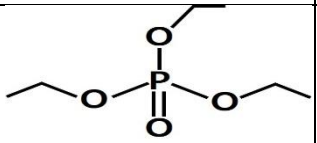
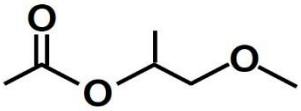
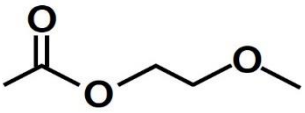
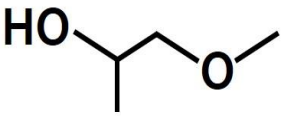
name	formula	Molecule weight (g/mol)	Boiling point (℃)	Density (g/mL)	Purity (%)	Company
Acetone		58.08	56	0.784	99.5	Daejung
K_2CO_3		138.21	Decomposes	2.43	99.5	Yakuri
MEA		61.08	170	1.01	99.5	Daejung
Glycerol		92.09	290	1.26	99.0	Samchun
DMSO		78.13	189	1.1	99.0	Samchun

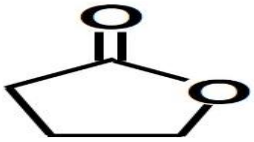
TEP		182.15	215	1.07	99.0	Daejung
PGME		90.1	120	0.92	99.0	Sigma

Water has a high carbon dioxide / methane selectivity but low carbon dioxide capacity. Therefore, in order to solve this disadvantages, experiments were conducted on solvents having high solubility of carbon dioxide. Carbon dioxide is known to have a relatively high solubility in solvents containing ether and carbonyl groups. Experiments were carried out in the same way using solvents with ether bond and carbonyl groups, and experiments were also conducted using solvents such as alcohols and glycol having hydroxyl groups. The pure solvents used in the experiments are as follows. Acetone, Ethanol, Ethylene glycol, 1-hexanol, 1-octanol, DEGDME (Diethyleneglycol dimethyl ether), DMF (N, N Dimethylformamide), NMP (N-methyl-2-pyrrolidone), Propylene glycol, PGMEA (Propylene glycol monomethyl ether acetate), EGMEA (ethylene glycol monomethyl ether acetate), PGME (propylene glycol methyl ether), TEP (triethyl phosphate) and GBL (r-butyrolactone). The structure and properties of each solvent are shown in the Table. 5.

Table. 5 Structure and physical properties of chemical used in pure solvent test

name	formula	Molecule weight (g/mol)	Boiling point (℃)	Density (g/mL)	Purity (%)	Functional group	Company
Acetone		58.08	56	0.784	99.5	Carbonyl	Daejung
Ethanol		46.07	78.37	0.789	99.5	Hydroxyl	Daejung
1-hexanol		102.16	157	0.814	98.0	Hydroxyl	Junsei

1-octanol		130.23	188	0.824	98.0	Hydroxyl	Junsei
EG		62.07	197.3	1.11	99.0	Hydroxyl	Daejung
PG		76.09	188.2	1.04	99.0	Hydroxyl	Junsei
DMF		73.09	153	0.944	99.0	Carbonyl	Sigma
NMP		99.13	202	1.03	99.5	Carbonyl	Daejung
TEP		182.15	215	1.07	99.0	Phosphate	Daejung
DEGDME		134.18	162	0.937	99.0	Ether	Sigma
PGMEA		90.1	120	0.970	99.0	Carbonyl Ether	Daejung
EGMEA		118.13	145	1.006	98.0	Carbonyl Ether	Daejung
PGME		90.1	120	0.916	98.0	Ether Hydroxyl	Daejung

GBL		86.09	204	1.13	99.0	Carbonyl Ether	Daejung

Experiments were carried out under artificial seawater conditions to determine whether seawater could be used without deterioration of performance using water's high selectivity to carbon dioxide and methane. It was an experiment aimed at confirming the possibility of using seawater for carbon dioxide absorption process. Experiments were carried out at various concentrations of artificial seawater. The amount of each chemical used in the experiment is shown in the Table. 6. Composition of artificial seawater condition was prepared with concentration of 18000, 36000, and 72000ppm respectively by reference. The solution was prepared considering the volume of the reactor and the density of the solution, and the experiment was conducted.

Table. 6 The amount of chemical used to make artificial seawater under each experimental condition

	18000ppm (g/640mL)	36000ppm (g/640mL)	72000ppm (g/640mL)
$NaCl$	7.850	15.699	31.398
$MgCl_2\ 6H_2O$	1.664	3.328	6.656
Na_2SO_4	1.309	2.618	5.235
$CaCl_2\ 2H_2O$	0.371	0.742	1.485
KCl	0.222	0.445	0.890
$NaHCO_3$	0.064	0.129	0.257
KBr	0.032	0.065	0.129
H_3BO_3	0.009	0.017	0.035
$SrCl_2\ 6H_2O$	0.008	0.016	0.032
NaF	0.001	0.002	0.004
Salt sum weight	11.53	23.06	46.12

Water	644.47	632.94	609.88
Sum	656	656	656

As a final experiment, acetone among the pure solvents used showed the best performance from various viewpoints. Based on these results, we conducted experiments on acetone solution. Mixing of acetone and solvent, mixing of acetone and NaI salt, and experiments on acetone / water / NaI were carried out. The conditions used in the experiment are as Table. 7.

Table. 7 Experimental conditions used in the acetone base solution

	Initial gas composition (%) CH_4 : CO_2	**Gas, solution volume ratio**	**NaI concentration in solution (wt%)**	**Water concentration in solution (wt%)**	**Acetone concentration in solution (wt%)**
1	**50:50**	**1:1**	**0**	**0**	**100**
2	**50:50**	**1:1**	**5**	**0**	**95**
3	**50:50**	**1:1**	**10**	**0**	**90**
4	**50:50**	**1:1**	**20**	**0**	**80**
5	**50:50**	**2:1**	**0**	**0**	**100**
6	**50:50**	**5:1**	**0**	**0**	**100**
7	**50:50**	**2:1**	**20**	**0**	**80**
8	**50:50**	**1:1**	**20**	**40**	**40**
9	**50:50**	**1:1**	**20**	**20**	**60**
10	**50:50**	**1:1**	**20**	**10**	**70**
11	**75:25**	**1:1**	**0**	**0**	**100**
12	**75:25**	**1:1**	**20**	**0**	**80**
13	**75:25**	**1:1**	**20**	**20**	**60**

1,5,6: volume ratio effect in pure acetone at the same composition

1,2,3,4: Effect of NaI concentration at the same composition and volume ratio

4,7,12: Effect of gas composition and volume ratio at the same NaI concentration

1,4,9 / 11,12,13: same composition, same volume ratio, composition mass ratio effect

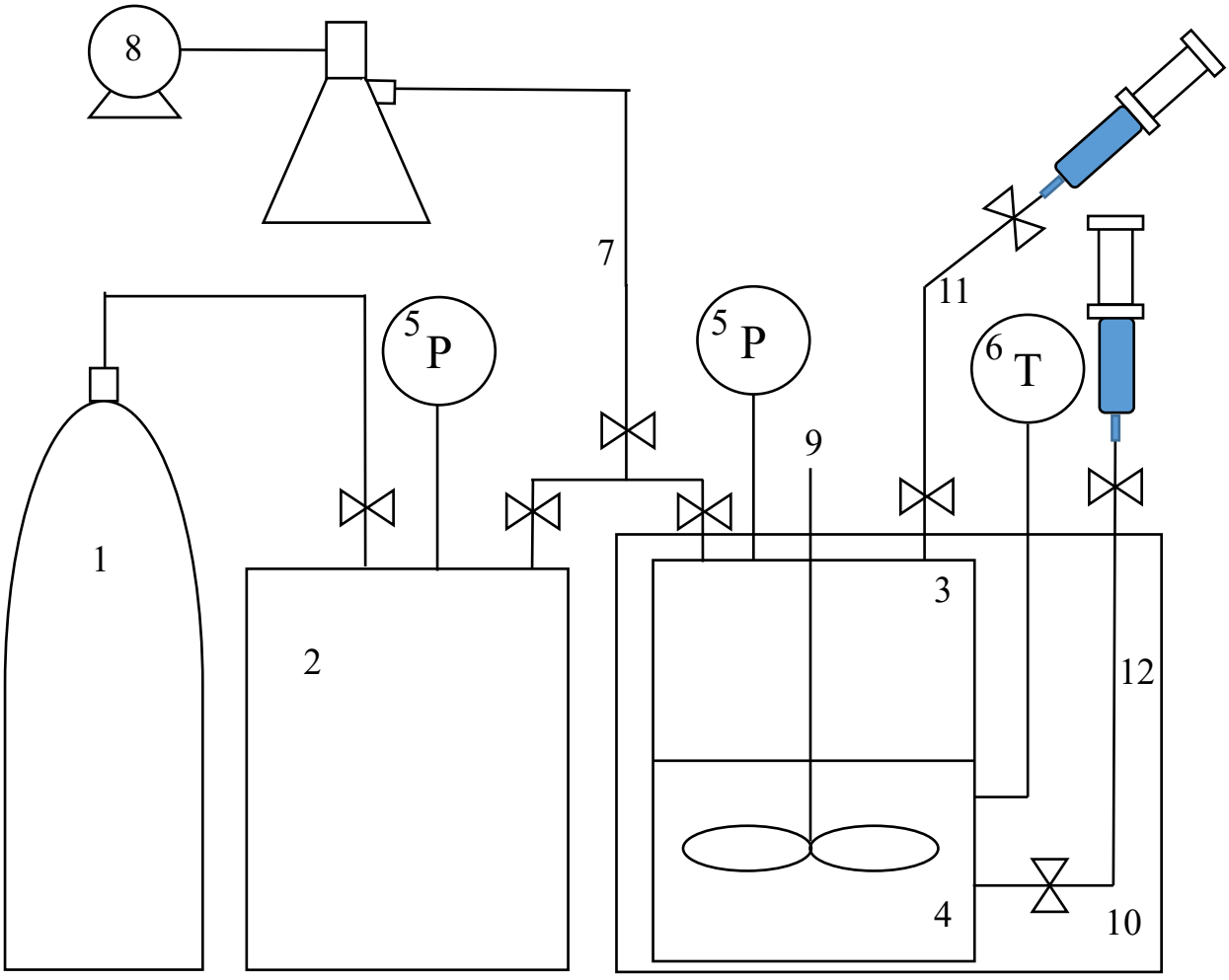


Fig. 7 Schematic diagram of the reactor used in the experiment

1. Gas container 2. Gas chamber 3. Reactor 4. Solution 5. Pressure gauge

6. Temperature probe 7. Vacuum purging line 8. Vacuum pump 9. Impeller

10. Water bath 11. Gas sampling line 12. Liquid sampling line

3.2 Experimental method

The experimental procedure is as Fig. 7. The gas and solution are poured into the reactor at the specified volume ratio, and the remaining gas is removed by vacuum purging with stirring until the gauge of the pressure gauge reaches -0.95 bar. In order to judge that the residual gas has been sufficiently removed, the reactor reaching -0.95 bar is stopped by stirring and vacuum purging, and left for 10 minutes to check leaking from the outside and pressure change due to the gas that has not come out of the solution. If there was no change in pressure for 10 minutes, the experiment was ready to begin. The gas is supplied to the gas chamber from the gas cylinder. The gas used in the experiment was a mixture of two gases, carbon dioxide and methane, which are mainly composed of biogas. The reason for injecting the gas into the reactor after supplying the gas to the gas chamber is to minimize the gas supply time so as to minimize the gas dissolution during the gas supply. Fill the reactor with a pressure that is at least twice the initial pressure specified in the gas chamber and open the valve connected to the reactor and within a short time (within 3 seconds) to the specified pressure. After supplying the gas to the specified pressure, close the valve and stir at 200 rpm. Log the pressure data over time in real time and observe the change in pressure. It was judged that the reaction reached a steady state when the pressure did not change above or below 0.01 bar for more than 10 minutes. The initial temperature of the reactor before the start of the reaction was set to 15 ° C ± 0.5 ° C. Experiments using water were conducted to determine the pressure and reaction time of the initial feed gas. It was observed that the pressure of the reactor decreased within 500 seconds and there was no change after that. The time taken for the reaction to be terminated in the reactor can be set as a criterion of the residence time when applied to a continuous process. Therefore, the reference time for this experiment was set to 40 minutes (2400 seconds), which means that the reaction has reached a sufficiently steady state.

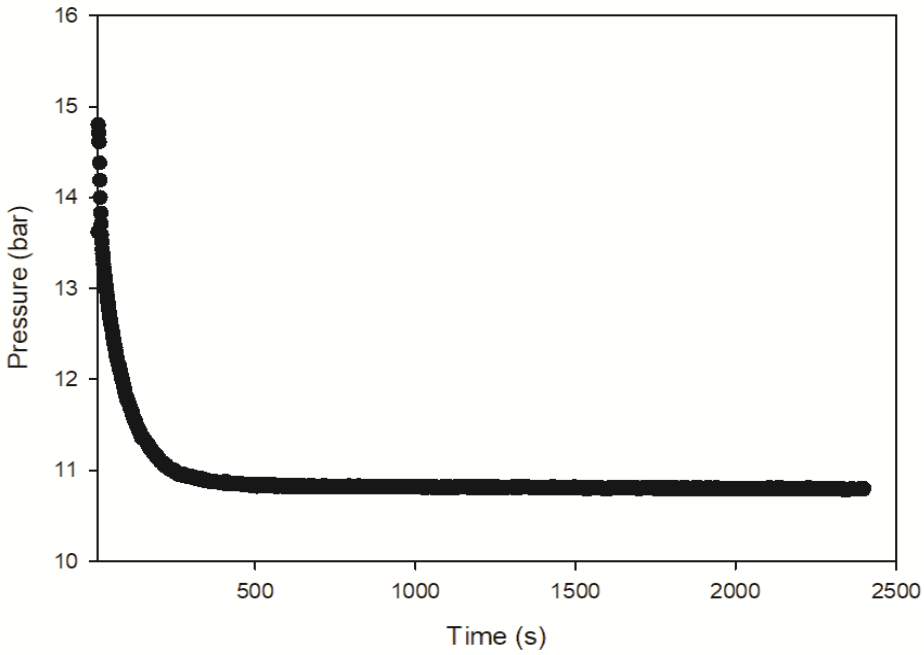


Fig. 8 Graph of pressure change over time in experiment with water at initial pressure 15 bar

All solutions were regenerated by vacuum purging and stirring until the pressure reached -0.95 bar at the end of each experiment. In order to judge the solvent suitable for the purpose of the experiment, four comparisons were made. In the given experimental conditions, the ratio of dissolved gas was calculated by the following equation in terms of the pressure reduction ratio.

Dissolved gas ratio (%) = $P_{equilibrium}$ / ($P_{initial}$ - P_{vacuum})

$P_{equilibrium}$: reactor pressure after reaction termination

$P_{initial}$: Initial pressure applied to the reactor

P_{vacuum} : reactor pressure in vacuum before start of reaction

After the reaction is completed, a double valve is used in the gas layer in the reactor to minimize the pressure loss and to sample a small amount of gas in the syringe. Seal the syringe with a parafilm and measure the composition of the gas sampled using gas chromatography. A small amount of the liquid in which the gas is dissolved in the syringe is sampled through the valve connected to the liquid layer. As the pressurized liquid is depressurized to normal pressure, the gas is degassed from the solution by the pressure difference in this process. The amount of gas to be degassed varies greatly depending on the properties of each solution. Similarly, the composition of the degassed AD gas was measured by gas chromatography (Agilent 7820A) and the volume of the degassed AD gas was measured using a

water substitution method. In order to compare the degassed AD gas volume of the solutions used in the experiments, the following equation was used.

Volume of degassed AD gas per unit volume (mL/mL) = V_{gas} / ($m_{solution}$ / $d_{solution}$)

V_{gas} : volume of AD gas degassed from solution (mL)

$m_{solution}$: weight of the sampled solution (g)

$d_{solution}$: Density of solution (g/mL)

Other experiments were conducted in the same way. Experimental conditions were as follows: the internal temperature of the reactor was 15℃ and the initial pressure was 15 bar. The volume ratio of the solution to the gas was 1: 1, and the experiment was carried out by varying the volume ratio in the experiment to determine the influence on the volume ratio. The composition of the solutions used in the experiments is described in the description of each result. Experimental data using water showed the average value measured during 5 cycles without water change, and all other solvents showed the average value measured during 3 cycles.

Chapter 4. Results

4.1 Water section

4.1.1 Effect of initial pressure

Water has a relatively high Henry's constant for carbon dioxide and low Henry's constant for nitrogen, oxygen and methane. Biogas separation experiments using pure water were carried out using the advantage of high selectivity for carbon dioxide and methane. The composition of biogas was 50% of carbon dioxide and 50% of methane. The temperature condition was fixed at 15℃ (± 0.5℃) to confirm the effect of initial pressure. Also, the volume ratio of water and gas in the reactor was fixed at 1:1 and initial pressurization pressure was set at 5, 10, and 15 bar. Experimental data were obtained by measuring the ratio of the dissolved gas, the composition of the remaining gas after the reaction, the composition of the degassed AD gas during the decompression of the water to atmospheric pressure, and the volume of the gas to be degassed when the pressure was finally reduced to normal pressure. All experimental data are summarized in the above order. Experiments on water were performed 5 times for each pressure, and water was reused through physical regeneration using vacuum purging and stirring without changing water at each condition. The experimental data are summarized by the mean value of 5 experimental results.

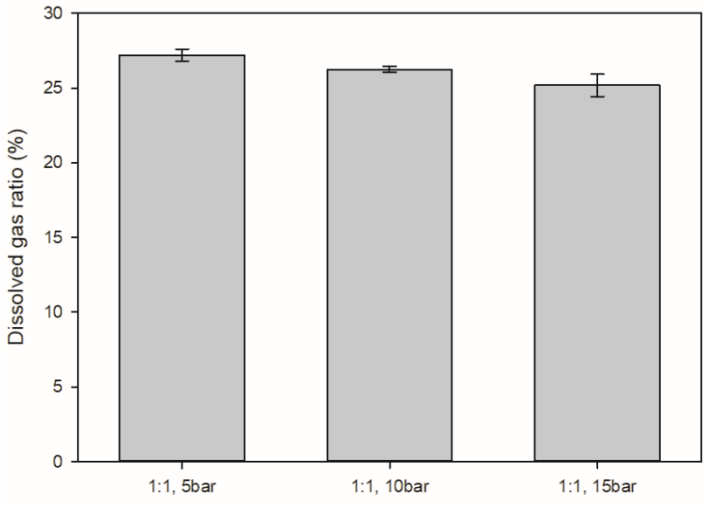


Fig. 9 Ratio of dissolved gas to initial pressure in pure water

Fig. 9 shows the ratio of dissolved gas to initial pressure difference. Since water follows Henry's law well, changes in initial pressure have found no significant change in the rate of dissolved gas.

Fig. 10 is the ratio of dissolved gas during five cycles when water was regenerated only by vacuum purging and stirring in the above experimental conditions.

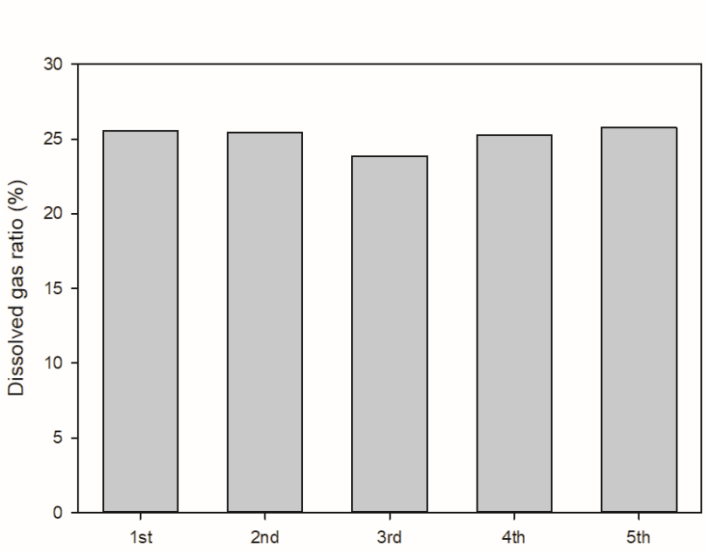


Fig. 10 Ratio of dissolved gas to water reuse cycle

No significant change in the gas absorption capacity of the water was observed, although the water was not replaced and continued to be used as a physical regeneration method. From this result, it can be confirmed that water can physically regenerate the gas and use it without deteriorating the performance. Therefore, for all experiments, the experiment was conducted to find a solvent that does not show a significant deterioration in performance even in repeated experiments, such as water, without using heating or other regeneration methods.

Next, the absorption selectivity of the gas of the water was evaluated through the composition of the remaining gas without dissolution after termination of the reaction at Fig. 11.
It was confirmed that the reaction was terminated at a constant rate regardless of the initial pressure when the composition of the residual gas after the reaction was terminated according to the initial pressure inside the reactor. As a result of the experiment using 50% carbon dioxide and 50% methane gas, the gas was separated by 60% of carbon dioxide and 40% of methane after the completion of the reaction. The results show that the water follows Henry's law well and the water is excellent in selectivity but not enough to absorb carbon dioxide.

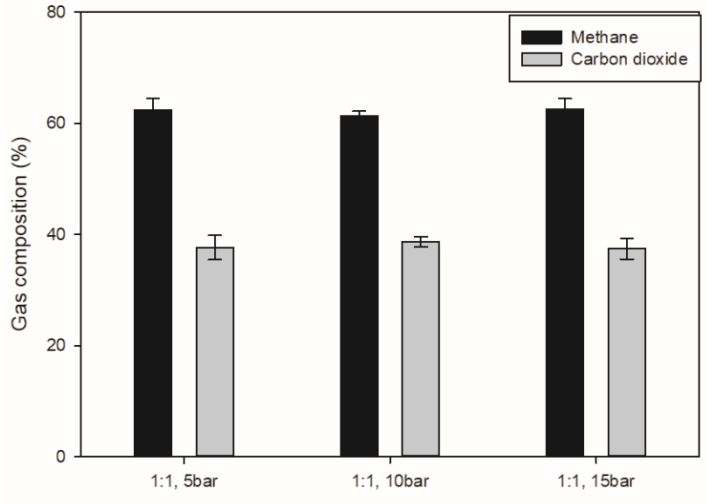


Fig. 11 Residual gas composition after reaction according to initial pressure in pure water

Fig. 12 shows the composition of the gas constituting the degassed AD gas by sampling the water after completion of the reaction. As the water was lowered from the high pressure inside the reactor to the normal pressure, the dissolved gas was degassed and the composition at that time was measured. Similar to the previous experimental results, the effect of initial pressure was not observed. All three cases of degassed carbon dioxide showed more than 90%.

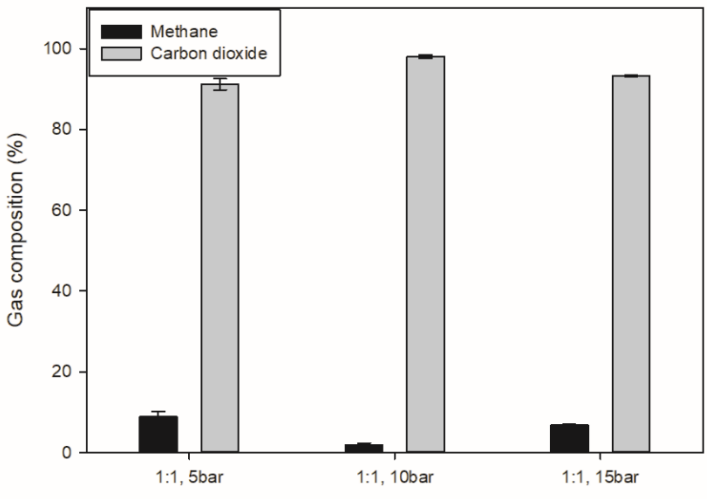


Fig. 12 Degassed AD gas composition at the initial pressure in pure water

From these results, it was confirmed that water has a great advantage in terms of recycling of captured carbon dioxide.

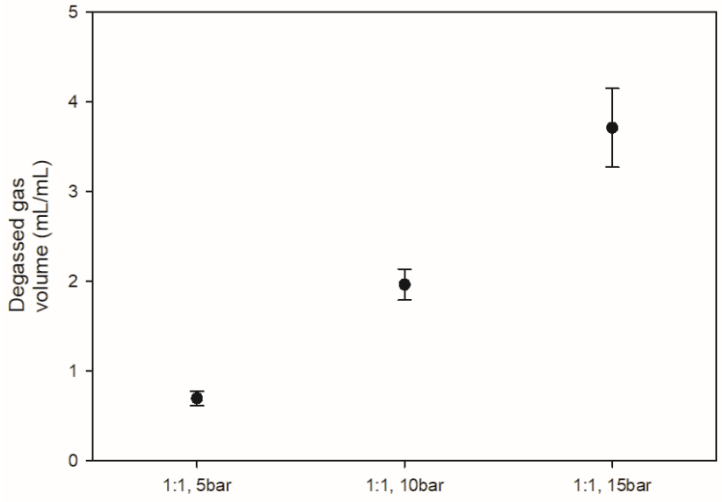


Fig. 13 Degassed AD gas volume at the initial pressure in pure water

Fig. 13 is the data of the volume of degassed AD gas when degassing the pressurized water at normal pressure. As expected, there was no significant difference in the composition of the degassed AD gas, but the amount of degassed AD gas varied. As the initial pressurized pressure increased, the partial pressure of each gas increased and the amount of dissolved gas increased proportionally. A similar tendency was also observed for the amount of degassed AD gas. Therefore, it was concluded that the higher the initial pressure, the better the recycling of carbon dioxide. The initial pressure of the gas was fixed at 15 bar and the volume ratio in the gas and water reactor was used as an experiment.

4.1.2 Effect of gas/water volume ratio

The initial pressure was fixed at 15 bar and the experiment was carried out using the volume ratio of water and gas as parameters. In Fig. 14, the influence of Henry's Law was confirmed again. In the batch reactor, the volume of water and the volume of gas are inversely proportional to each other, so that as the volume of water increases, the amount of gas supplied decreases. As the volume of water increased, the proportion of dissolved gas inside the reactor tended to increase. This is because the amount of gas that can be dissolved increases as the volume of water increases.

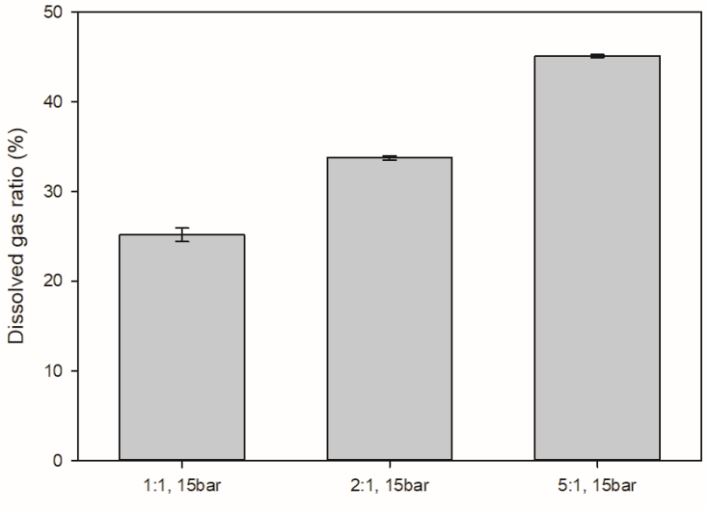


Fig. 14 Ratio of dissolved gas to water and gas volume ratio at an initial pressure of 15 bar

Fig. 15 shows the composition of the residual gas after the reaction when the volume ratio of water and gas is used as a parameter. As the volume of gas and water in the reactor was varied at constant pressure, the amount of residual carbon dioxide decreased to 20% as the amount of water increased. The control of the volume ratio of water and gas was considered to be one of the variables that could be considered in terms of carbon dioxide removal.

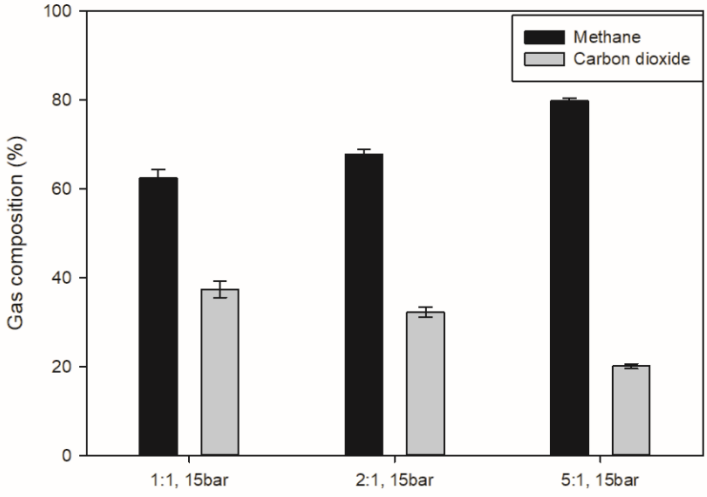


Fig. 15 Residual gas composition by water and gas volume ratio at the initial pressure of 15 bar

Fig. 16 shows the composition of degassed AD gas when the volume ratio of water and gas is used as a parameter. The degassed AD gas composition was observed when the initial pressure was fixed and the

volume ratio of water to water in the mixed gas was increased. As the volume of water increased, the proportion of methane in the degassed AD gas increased and the proportion of carbon dioxide decreased relatively. In terms of recycling of degassed carbon dioxide, it is judged that the volume ratio of water is low.

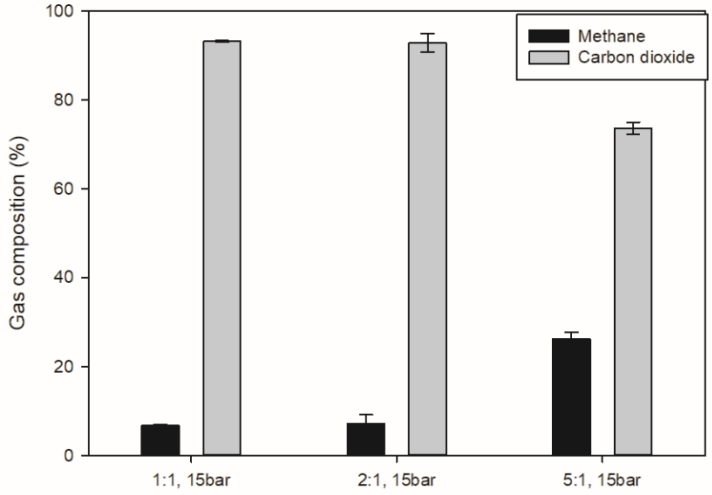


Fig. 16 Degassed AD gas composition by water and gas volume ratio at the initial pressure of 15 bar

Finally, Fig. 17 shows the amount of degassed AD gas volume according to the volume ratio of water and gas at the same initial pressure. As the amount of water increases, the volume of dissolved gas decreases with the amount of water, so that the volume of degassed AD gas decreases. Therefore, when considering the above four aspects, it is determined that the conditions suitable for the continuous process are suitable when the volume ratio of water to gas is 1: 1 and the initial pressure is 15 bar, which shows both excellent composition and volume of degassed AD gas. In order to compare the lengths and disadvantages of all experiments, the volume ratio of gas and solution was 1: 1, initial pressure was 15 bar, and initial temperature was 15℃.

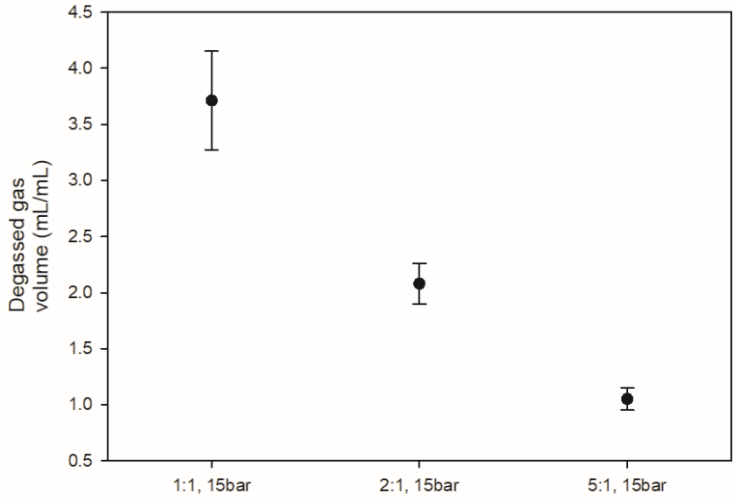


Fig. 17 Degassed AD gas volume by water and gas volume ratio at the initial pressure of 15 bar

4.2 Aqueous solution section

4.2.1 Effect of functional group

Through experiments on water, it was confirmed that water has an advantage in terms of recycling of dissolved carbon dioxide. In order to improve the low carbon dioxide capacity which is a disadvantage of water, experiments using an aqueous solution were carried out. The aqueous solutions used in this experiment were aqueous solutions of monoethanolamine (MEA) and potassium carbonate (K_2CO_3), Dimethyl sulfoxide (DMSO) with S = O group, Glycerol with hydroxyl group, acetone with C = O group, propylene glycol methyl ether (PGME) with ether bond and hydroxyl group, and triethyl phosphate (TEP) with P = O group. All the aqueous solutions were prepared with 30wt% aqueous solutions.

Fig. 18 (a) shows the ratio of dissolved gas in a strong aqueous base solution. MEA and K_2CO_3 aqueous solutions, which are strong base solutions, showed higher dissolution rates than other aqueous solutions. Because of the chemical reaction with carbon dioxide mainly through acid and base reaction, both of the strong base aqueous solutions exhibited a high dissolved gas ratio. Fig. 18 (b) shows the ratio of dissolved gas in the organic solvent solution. The aqueous solutions other than the strong base aqueous solutions used in the experiments showed a lower dissolved ratio compared to the pure water, regardless of the functional groups. This is because the bond between water and each solvent has the effect of further reducing the binding of water, carbon dioxide, solvent and carbon dioxide. Therefore, it was

judged that the mixture of solvent and water and used in the form of aqueous solution did not meet the purpose of the experiment.

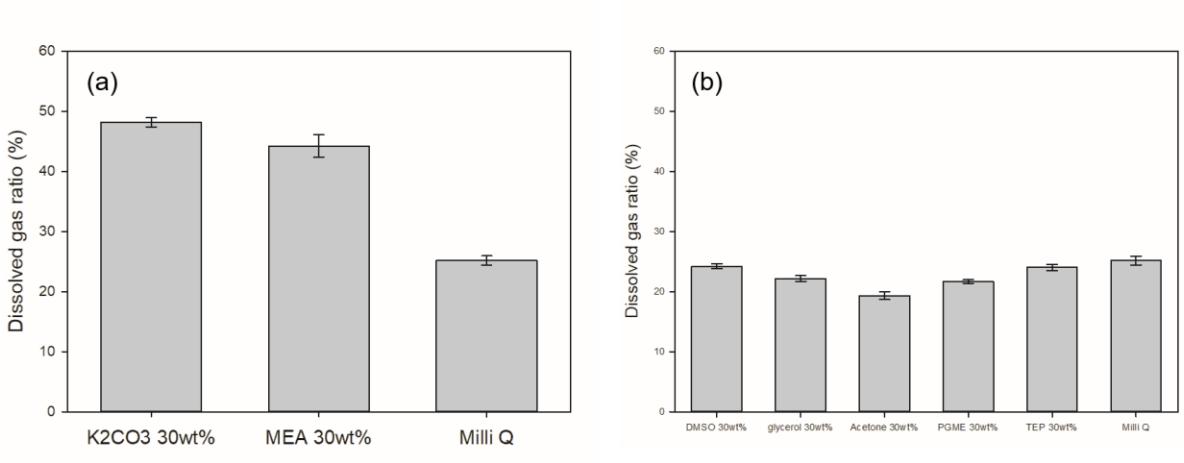


Fig. 18 (a) Strong base aqueous solution (K_2CO_3, MEA) (b) organic solvent aqueous solution (DMSO, Glycerol, Acetone, PGME, TEP) the ratio of the gas dissolved in each solution at the initial pressure

The gas composition after the reaction of aqueous solution was observed at Fig. 19. As expected, both K_2CO_3 and aqueous MEA solutions were able to remove most of the initially supplied carbon dioxide. Both of these cases had significantly higher carbon dioxide capacity than water and thus were found to be very good in terms of carbon dioxide removal. In the case of the aqueous solution except the strong base, the ratio of dissolved gas was lower than that of pure water, but the removal rate of the carbon dioxide in the aqueous solution was similar to that of the previous case. The aqueous solution was also found to have no advantage when based on this experimental data.

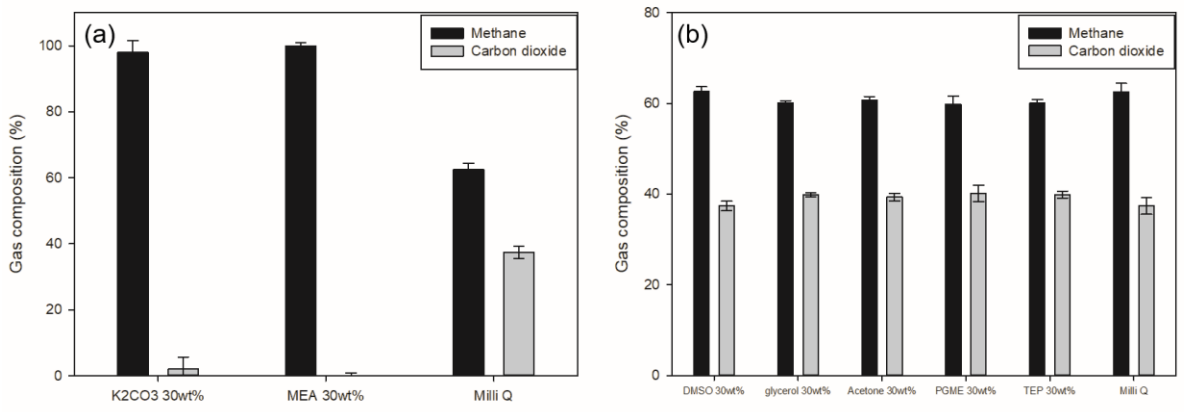


Fig. 19 (a) Strong base aqueous solution (K_2CO_3, MEA), (b) organic solvent aqueous solution

(DMSO, Glycerol, Acetone, PGME, TEP) Residual gas composition in aqueous solution at the initial pressure of 15 bar, 1:1 ratio of solution: gas volume

In Fig. 20, the composition of the gas generated by the pressure difference was measured in the process of reducing the pressure inside the pressurized reactor to normal pressure after the reaction. In the case of K_2CO_3 and MEA strong base aqueous solution at Fig. 20 (a), the degassed AD gas hardly occurred during decompression to normal pressure. Therefore, it was judged that the composition of the degassed AD gas could not be measured and it did not meet the purpose of carbon dioxide recycling for the purpose of this experiment. The organic solvent aqueous solutions showed a degassed carbon dioxide composition that was almost the same as or slightly lower than that of pure water at Fig. 20 (b). From this experiment it was also found that the aqueous solution had no other advantage.

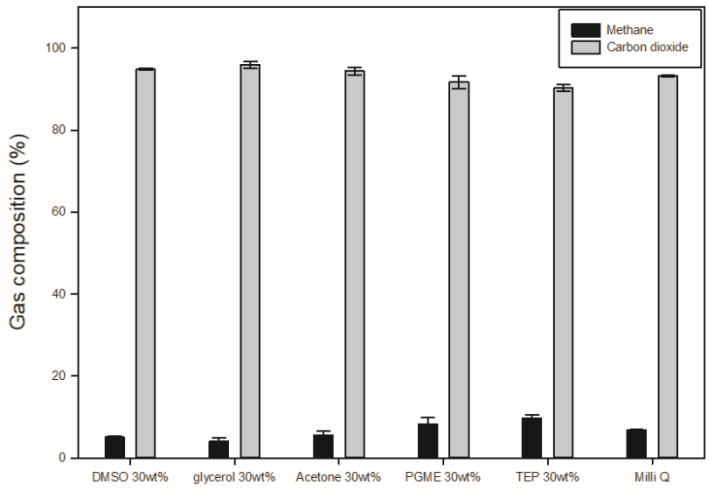


Fig. 20 Organic solvent aqueous solution (DMSO, Glycerol, Acetone, PGME, TEP) degassed AD gas composition in aqueous solution at the initial pressure of 15 bar, 1:1 ratio of solution: gas volume

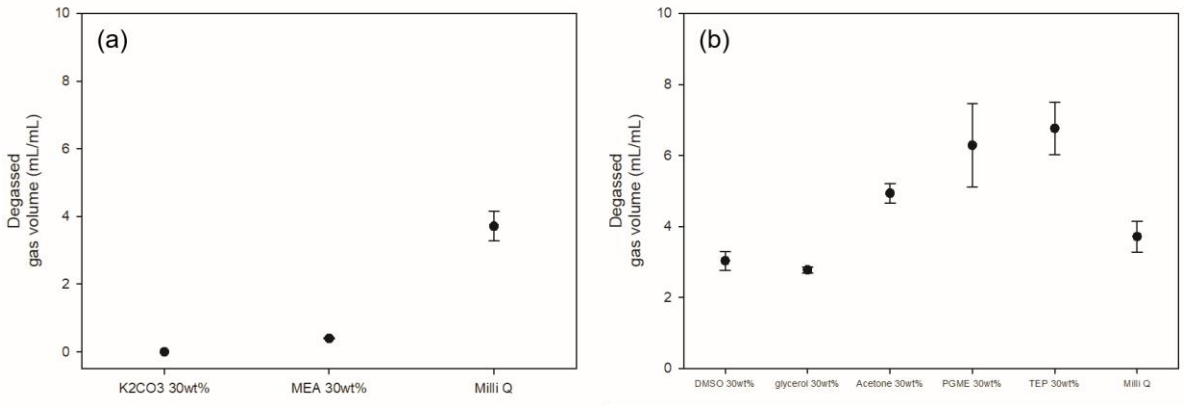


Fig. 21 (a) Strong base aqueous solution (K_2CO_3, MEA) (b) organic solvent aqueous solution (DMSO, Glycerol, Acetone, PGME, TEP) degassed AD gas volume in aqueous solution at the initial pressure of 15 bar, 1:1 ratio of solution: gas volume

Fig. 21 shows the measured volume of degassed AD gas during decompression at normal pressure. The pressurized aqueous solution was collected from the reactor and the volume of the collected gas was measured by the water substitution method. K_2CO_3 showed almost no degassed AD gas and only very small amount of gas was collected in MEA. From this result, it can be understood that it is not solved only by increasing or decreasing the pressure in order to degas the carbon dioxide bound by the acid or base reaction from the aqueous solution. The reuse of the aqueous solution of the strong base was confirmed to require heating through a large energy consumption.

The volume of degassed AD gas for aqueous organic solvent solutions was also measured at Fig. 21 (b). Likewise, it was measured using a water substitution method, and solvents such as acetone, PGME and TEP were degassed in a larger amount than in water. These results show that the degassed AD gas may be present depending on the increase or decrease of the pressure based on the physical absorption, which was the object of this experiment, and showed the possibility of the application of the continuous process in the future. Based on these experiments, we compared the advantages and disadvantages of pure solvents with water.

4.3 Pure solvent section

4.3.1 Effect of functional group

Experiments were conducted on solvents with various functional groups. It was aimed to observe the effect of functional groups. Experiments were carried out using pure solvents and proceeded in the same way. Ethanol and acetone were not subjected to vacuum purging because their vapor pressure was very high. Regeneration was carried out by stirring and increasing or decreasing the pressure. The experimental data are shown for four factors. Functional groups were classified into alcohol, glycol, ether & carbonyl group, carbonyl group and water. For one solvent with the same functional group, the figure is shown for the purpose of comparing the results according to the effect of the functional groups. Experimental data on other solvents are summarized in tables.

The ratio of dissolved gas to each functional group is shown in the Fig. 22. Except for Glycol, the other solvents showed a much higher pressure reduction ratio than water. Ethylene glycol and propylene glycol showed lower dissolved gas ratio than other solvents and the reaction time to equilibrium was longer than other solvents. Unlike the solvents of the alcohol type used, there are more OHs that can react with carbon dioxide because of lower molecular weight and more OH bonds. However, it was concluded that OH groups were more soluble in glycol than in alcohol because OH bonds formed hydrogen bonds with each other and deprived of a part that could react with carbon dioxide. Compared with ethylene glycol and propylene glycol, the dissolved gas ratio of propylene glycol was higher than that of ethylene glycol because the number of OH in the propylene glycol having a relatively higher molecular weight is smaller when the same volume of solvent is used, It was judged to be the result of more reaction with carbon dioxide than bonding.

Alcohol and acetone showed similar values, and EGMEA with both ether and carbonyl groups showed higher ratio of dissolved gas. Except for glycols, the solvents with functional groups of alcohol, ether & carbonyl group and carbonyl group showed similar gas dissolution rates. In Fig. 23, the compositions of the undissolved gases were compared after the reaction.

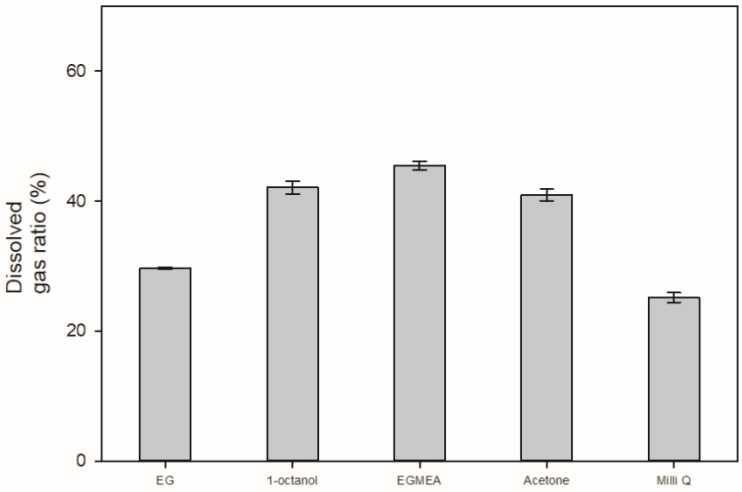


Fig. 22 Ratio of dissolved gas in pure solvent

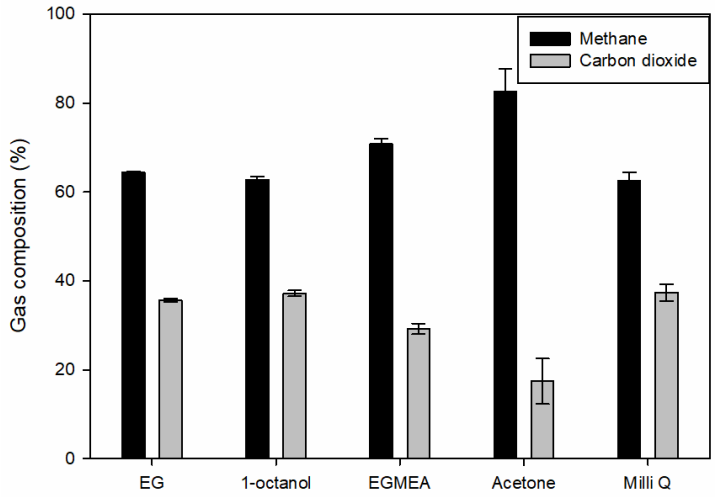


Fig. 23 Residual gas composition gas after reaction in pure solvent

Ethylene glycol and 1-octanol showed similar results to water, while EGMEA showed a residual methane and carbon dioxide composition of about 70:30. Based on the above dissolved gas ratio results, the results were similar because of the low solubility of ethylene glycol and water to carbon dioxide itself, and the dissolution rates of 1-octanol and EGMEA were much higher compared to water, It was judged that the above results were obtained because the solubility in methane was high with respect to the composition observed somewhat higher. These properties are considered to be unsuitable for the purpose of this experiment because they have disadvantages in terms of selectivity, an important factor in gas separation. Acetone showed a high amount of carbon dioxide removal when compared to other solvents and residual methane and carbon dioxide composition of about 80:20 was observed. Acetone

was found to have significant advantages over other solvents in terms of carbon dioxide removal. In Fig. 24, the composition of the degassed AD gas was measured from the decompression process in the solvent.

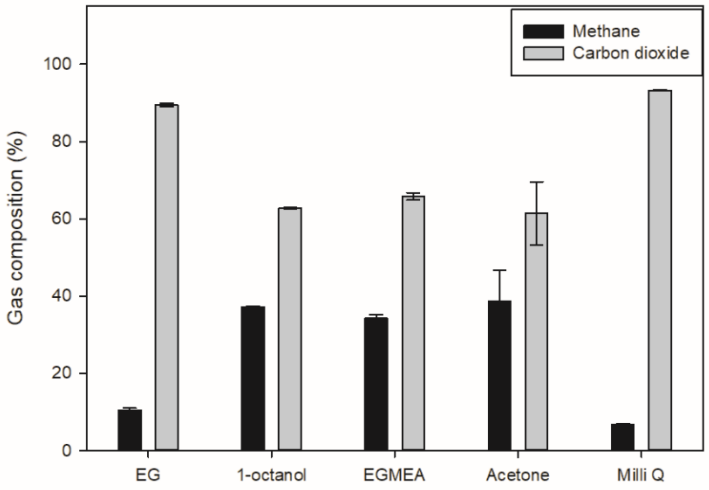


Fig. 24 Degassed AD gas composition after reaction in pure solvent

The results showed that the trends agreed with the above were consistent. The solubility of water and ethylene glycol was lower than that of other solvents, but the solubility of methane was lower than that of carbon dioxide. Therefore, it was confirmed that the ratio of carbon dioxide in the composition of the degassed AD gas was high. Both 1-octanol, EGMEA, and acetone have relatively low methane solubility and relatively low carbon dioxide composition in the degassed AD gas. A method for increasing the degassed composition of carbon dioxide was deemed necessary. Finally, the volume of degassed AD gas was measured in this experiment at Fig. 25.

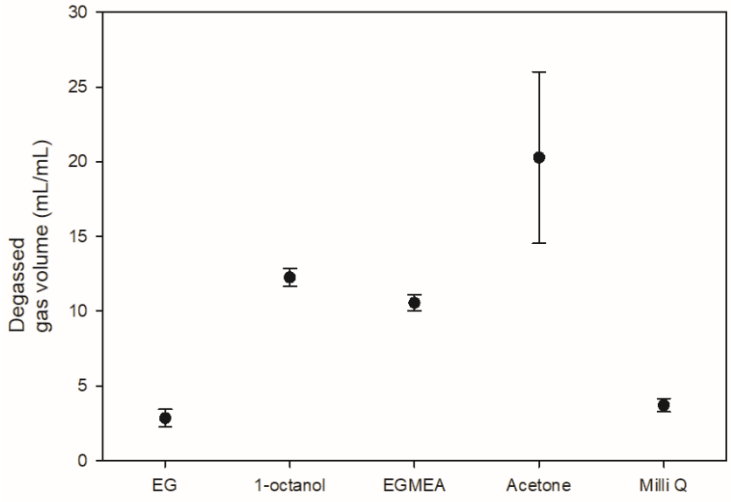


Fig. 25 Degassed AD gas volume after reaction in pure solvent

Fig. 25 shows the volume of AD gas degassed in each solvent. Water and ethylene glycol showed similar values, and 1-octanol and EGMEA showed values between 10 and 15 mL per mL of solvent. Acetone had the largest amount of solvents used in the experiment when more than 20 mL of gas had been degassed. This is because acetone's ability to degas the dissolved gas was superior to other solvents. However, it was thought that the decompression of the pressurized acetone could also cause the evaporation of acetone due to the low vapor pressure of acetone. Combining the above four figures, we have determined that acetone is suitable for the purpose of the experiment and conducted experiments to solve the disadvantage of acetone which is low carbon dioxide / methane selectivity of degassed AD gas. The results for all pure solvents used in the experiments are summarized in the Table. 8.

Table. 8 Experimental data summarization for pure solvents

	Dissolved gas ratio (%)	Residual gas composition (CO_2 %)	Degassed AD gas composition (CO_2 %)	Degassed AD gas volume (mL/mL)	Functional Group
EG	29.69±0.17	35.67±0.34	89.48±0.51	2.84±0.59	Hydroxyl
PG	36.42	36.73	80.71	3.62	Hydroxyl
1-hexanol	41.94±0.01	35.23±1.61	61.03±0.32	12.06±2.10	Hydroxyl
1-octanol	42.11±1.01	37.22±0.66	62.78±0.18	12.26±0.60	Hydroxyl
1-ethanol	42.12±2.37	32.08±9.90	70.40±1.71	N.D	Hydroxyl
Acetone	40.99±0.91	17.41±5.09	61.39±8.15	21.83±0.82	Carbonyl
DMF	43.87±2.07	21.97±6.48	68.02±0.22	9.09±0.66	Carbonyl
NMP	43.95±0.63	27.38±0.72	72.01±1.16	6.83±0.75	Carbonyl
TEP	45.64±0.69	28.14±1.18	66.00±2.24	10.93±0.53	Phosphate
DEGDME	46.02±2.02	25.51±0.71	64.54±1.07	12.28±1.79	Ether
PGMEA	47.00±0.81	25.25±2.12	62.84±0.89	17.95	Carbonyl, ether
EGEEA	45.52±0.66	29.21±1.19	65.79±0.95	10.57±0.52	Carbonyl, ether
GBL	44.15±1.06	27.35±1.02	74.45±1.48	6.45±0.66	Carbonyl, ether
PGME	44.79±1.34	23.20±3.41	64.04±0.78	9.50±0.89	Ether, alcohol

4.4 Artificial sea water section

4.4.1 Effect of salt concentration in artificial sea water

Experiments using artificial seawater were conducted to confirm the possibility that seawater existing on the Earth could be used for carbon dioxide absorption without going through the purification process. The purpose of this experiment was to observe the tendency of the addition of salt in solution. Fig. 26 shows the ratio of dissolved gas when compared to water under artificial seawater conditions. The rate of dissolved gas tended to decrease with increasing concentration of salt in artificial sea water condition. However, up to 36000 ppm did not show a significant decrease compared with pure water. It was observed that the rate of reduction of dissolved gas was increased when 72000 ppm of salt was added. From these results, it was concluded that the addition of a small amount of salt may not significantly reduce the ability of the solution to absorb carbon dioxide.

Similar trends were observed in all cases when the residual gas composition was observed after the reaction. Compared to pure water, it showed almost similar methane and carbon dioxide composition. Fig. 27 confirm once again that salt does not significantly reduce the carbon dioxide uptake of the solution.

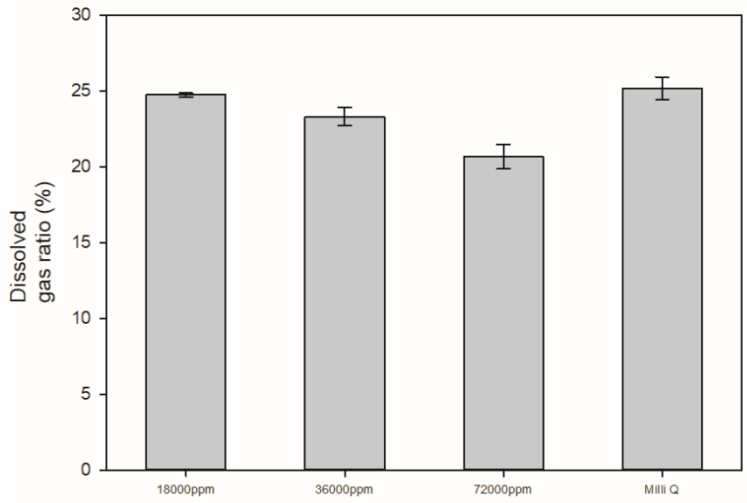


Fig. 26 Ratio of dissolved gas in artificial sea water

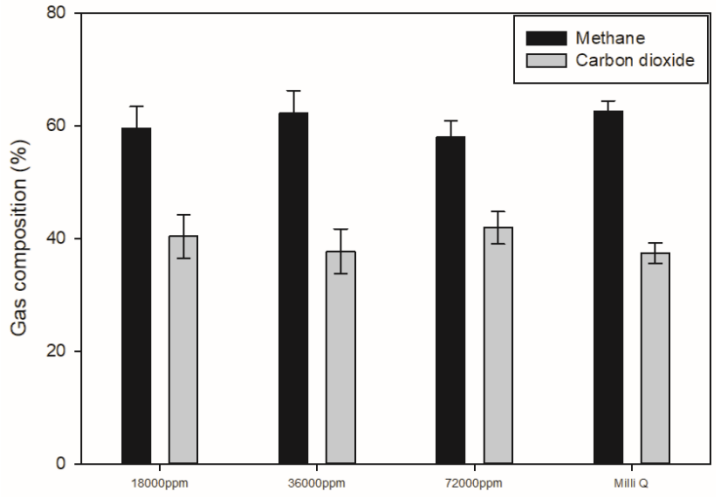


Fig. 27 Residual gas composition gas after reaction in artificial sea water

Similarly, the composition of the degassed AD gas was observed at Fig. 28. It was observed that the ratio of degassed carbon dioxide increased from pure water under the condition of salt added artificial seawater. Although the increase in the numerical value is not great, the rate of increase in the selectivity of carbon dioxide and methane is high. This result is due to the fact that the salt has the effect of pushing out the carbon dioxide dissolved in the water due to the salting out effect while being present in the water. Therefore, it was concluded that the addition of salt could have advantages in terms of degassing for carbon dioxide recycling, which is the purpose of this experiment.

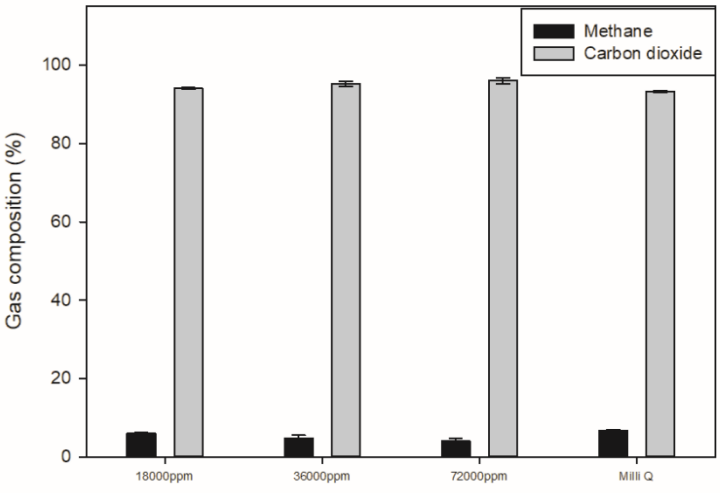


Fig. 28 Degassed AD gas composition after reaction in artificial sea

The volume of degassed AD gas was compared with pure water at Fig. 29. It was observed that the artificial seawater condition was slightly lower than that of pure water, but there was generally no significant difference. As a result of this data, it was confirmed that the addition of salt could play a positive role in the purpose of the experiment.

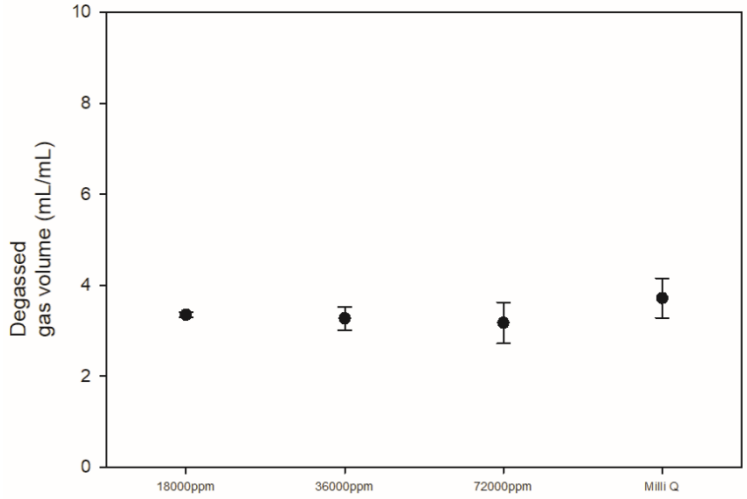


Fig. 29 Degassed AD gas volume after reaction in artificial sea

4.5 Acetone base solution section

Acetone was found to have many advantages over other solvents and acetone was selected. Acetone has the disadvantage of high volatility due to high vapor pressure and a high ratio of methane occupying the degassed AD gas. Therefore, we devised a method to solve these problems. Experiments were conducted using solutions based on acetone.

4.5.1 Effect of gas/liquid ratio in pure acetone

Experiments were carried out with respect to the ratio of acetone to gas in the reactor as parameters, in order to determine whether acetone follows the tendency of physical absorption.

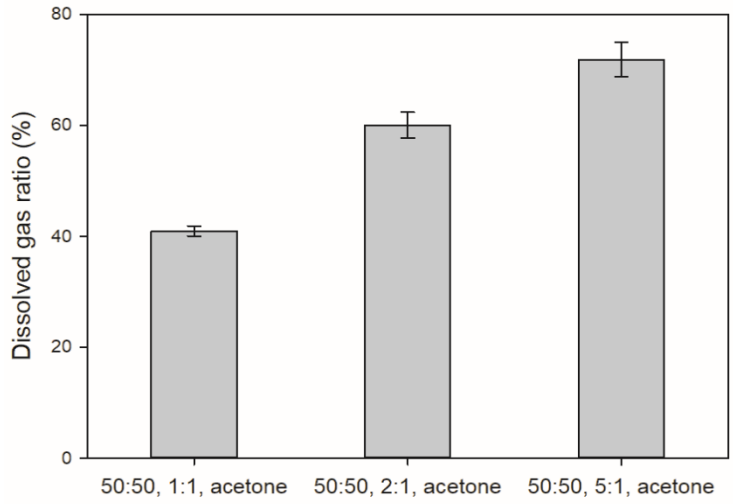


Fig. 30 Ratio of dissolved gas to the volume ratio of acetone to gas

The ratio of dissolved gas to gas composition and volume ratio is shown Fig. 30. As the amount of acetone increased and the amount of gas decreased, the proportion of dissolved gas tended to increase as the tendency of water. These results show that acetone also follows Henry's law, which is proportional to solubility in partial pressure of gas.

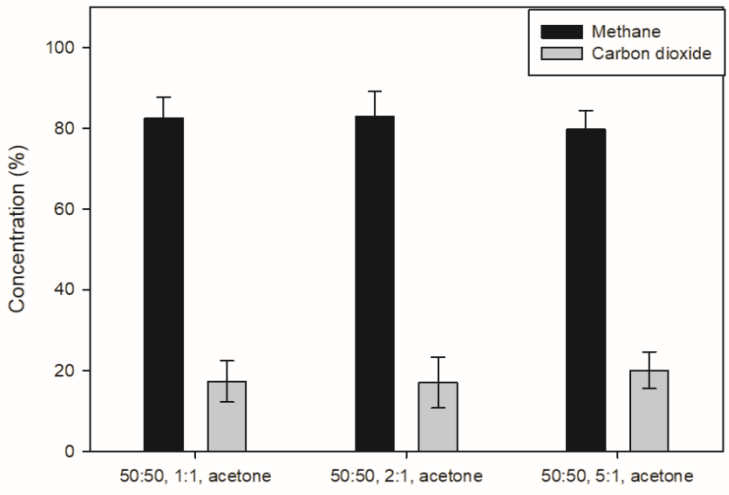


Fig. 31 Residual gas composition after reaction in acetone

After the reaction reached equilibrium, the composition of the residual gas was measured at Fig. 31. In the water experiment, the composition of the remaining carbon dioxide tended to decrease as the volume ratio of water increased. In the case of acetone, however, the tendency was almost constant regardless of the volume ratio. This is because the absorption capacity of acetone is larger than that of water, and it is judged that acetone volume of 1:1 can sufficiently dissolve carbon dioxide. It was confirmed that 50:50 mixed methane / carbon dioxide gas can be separated at a ratio of about 80:20 under the acetone condition, and it was confirmed that carbon dioxide can be sufficiently treated with acetone absorption capacity even under the condition of 1:1.

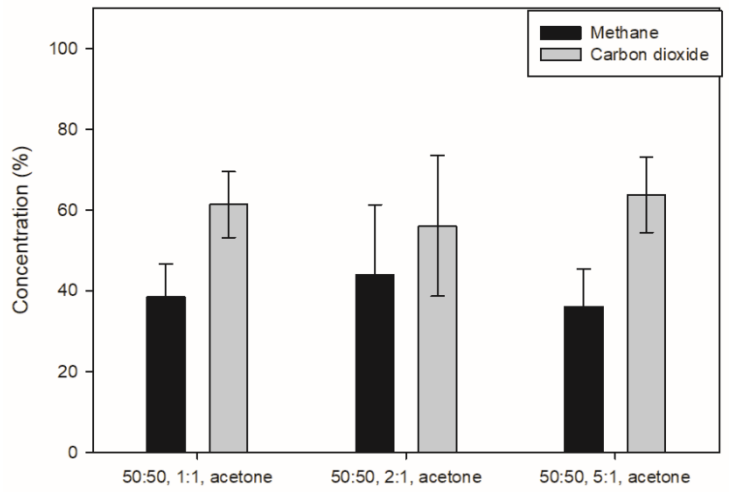


Fig. 32 Degassed AD gas composition after reaction in acetone

Previously, most solvents, including acetone, showed less selectivity for degassed AD gases than water. This is because the amount of carbon dioxide that can be absorbed is large, but the amount of methane that can be absorbed is also relatively high. Fig. 32 also show that acetone occupies a somewhat higher proportion of methane in the degassed AD gas. In addition, almost constant methane and carbon dioxide degassed ratios were observed regardless of the volume ratio of gas and acetone. From these results, it was once again confirmed that acetone was followed by physical absorption.

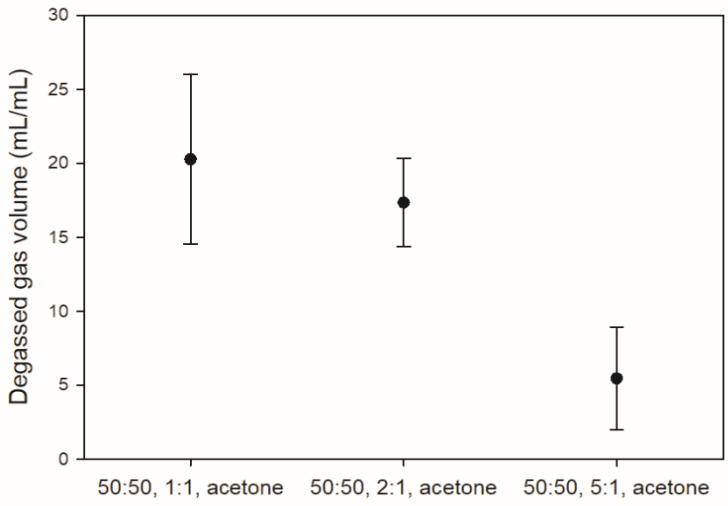


Fig. 33 Degassed AD gas volume after reaction in acetone

The volume of degassed AD gas was measured according to the volume ratio of acetone and gas in Fig. 33. The results of this experiment were similar to those of water. As the amount of gas is reduced and the amount of acetone is increased, the volume of degassed AD gas tends to decrease because the amount of gas dissolved in the same unit mass of acetone is less, as in the case of water. Therefore, it is considered that the ratio of 1:1 volume ratio of gas and liquid is the most ideal, and the experiment was conducted to overcome the disadvantages of the composition of degassed AD gas.

4.5.2 Effect of salt concentration in acetone solution

The direction of the experiment was set through experiments on pure Acetone. Acetone's high carbon dioxide absorption capacity and good follow-up properties of physical absorption, and its ability to degas a large amount of gas when it is degassed during decompression can be used as a good advantage considering the continuous process. However, it was confirmed that the proportion of methane in the

composition of the degassed AD gas is high. Acetone as a mixed solution to solve this problem. Experimental results of the artificial seawater condition showed that when the salt was added to the solution, the carbon dioxide treatment ability of the solution was not significantly reduced, but the higher the concentration of carbon dioxide in the degassed AD gas was possible. Therefore, it was confirmed whether the same effect could be obtained by adding salt to the acetone solution. Acetone shows low solubility for most salts. However, it was confirmed that NaI had high solubility and NaI concentration was varied. The concentration of NaI used was 5 wt%, 10 wt%, and 20 wt%, considering solubility.

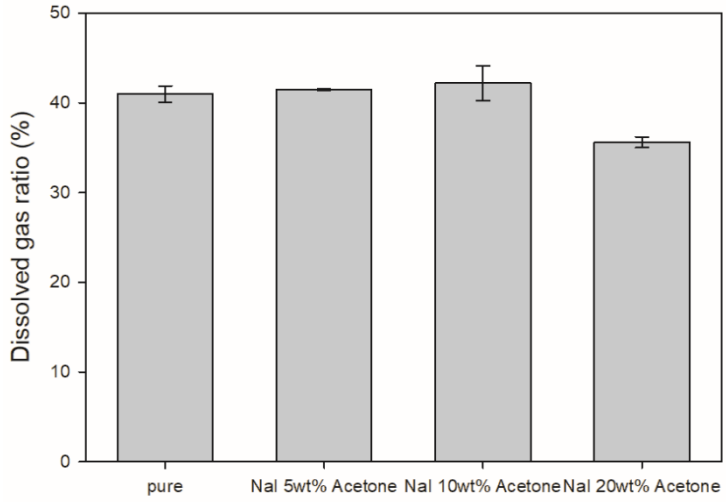


Fig. 34 Ratio of dissolved gas in acetone solution to NaI concentration

The experimental results of Pure acetone and acetone solutions were compared. Acetone solution containing 5wt% and 10wt% of NaI showed no significant difference in the dissolved ratio of gas at Fig. 34. It was observed that the ratio of the dissolved gas in the 20wt% acetone solution was slightly decreased. The results of this experiment were similar to those of artificial seawater and it was confirmed that the addition of appropriate salt did not cause a large decrease in the amount of dissolved gas.

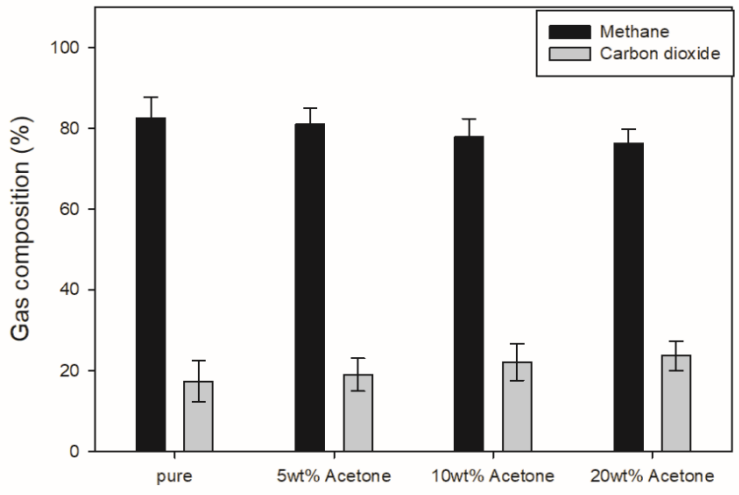


Fig. 35 Residual gas composition after reaction in acetone solution according to NaI concentration

After the reaction was completed, the composition of the residual gas was confirmed at Fig. 35. As the NaI concentration increased, the residual ratio of carbon dioxide increased slightly and the residual ratio of methane tended to decrease slightly. As a result, the gas absorption performance of the acetone solution was not significantly decreased.

Next, the effect of degassed AD gas on NaI concentration was confirmed at Fig. 36. Pure acetone and 5 wt% acetone showed no significant difference in the composition of the two gases. However, as the concentration of NaI increased to 10 wt% and 20 wt%, the composition of degassed carbon dioxide tended to increase. From the results, it was found that the addition of salt was similar to that of the previous artificial seawater test, which could help to degas the carbon dioxide, and that the ratio of degassed methane and carbon dioxide of 40:60 in pure acetone was improved to more than 30:70 in 20 wt% acetone.

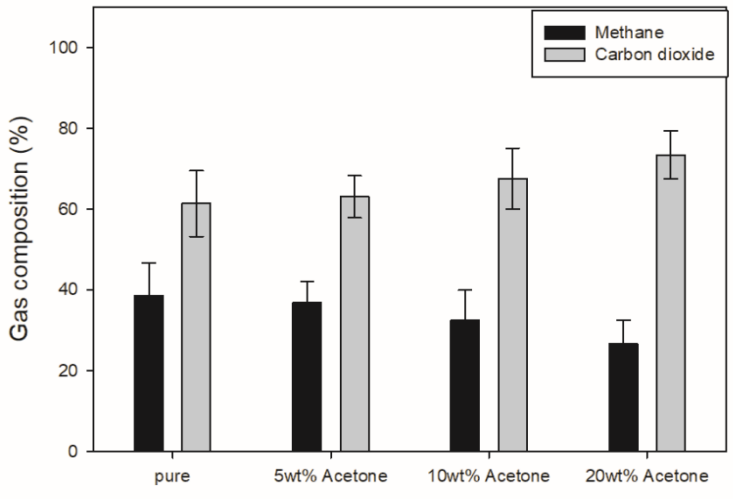


Fig. 36 Degassed AD gas composition in acetone solution according to NaI concentration

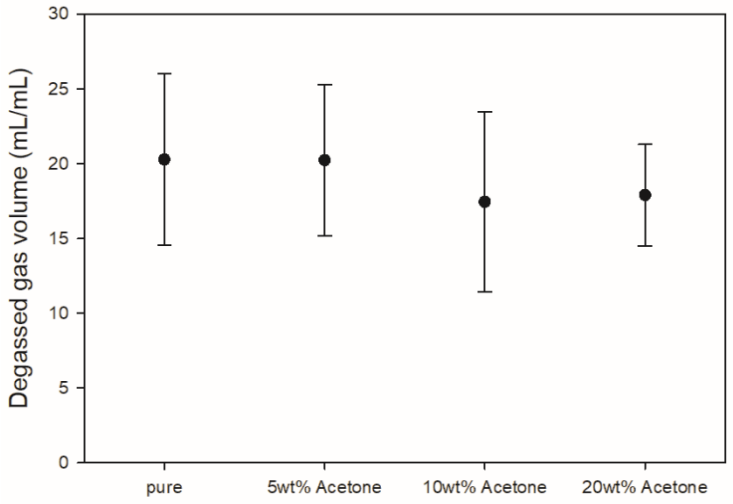


Fig. 37 Degassed AD gas volume in acetone solution according to NaI concentration

Finally, the results of the volume of degassed AD gas were confirmed for this experiment at Fig. 37. The carbon dioxide ratio of the degassed AD gas was increased, but when the results of acetone containing pure acetone and NaI were compared, it was confirmed that NaI salt did not significantly decrease the performance of the solution. In conclusion, the results of the experiment with NaI concentration showed that the increase of the concentration of NaI does not cause a large decrease of the dissolved carbon dioxide composition after the reaction and the ratio of the dissolved gas, and can improve the ratio of carbon dioxide in the degassed AD gas. Therefore, the NaI concentration was fixed at 20 wt% and the following experiment was conducted.

4.5.3 Effect of gas/liquid ratio, initial gas composition in NaI 20 wt% acetone solution

From the previous experiments, it was confirmed that the addition of NaI salt can increase the ratio of carbon dioxide in the composition of degassed AD gas, which is a disadvantage of acetone. This experiment was carried out to investigate the tendency of 20 wt% NaI acetone solution according to the volume ratio of gas and solution and composition of the initial feed gas. Experimental conditions were 1:1 and 2:1 volume ratio of solution and gas at 50:50 methane and carbon dioxide composition. Experiments were carried out on 1:1 volume ratio of solution and gas under the conditions of methane and carbon dioxide composition 75:25. The results of the ratio of dissolved gas in each case are as Fig. 38.

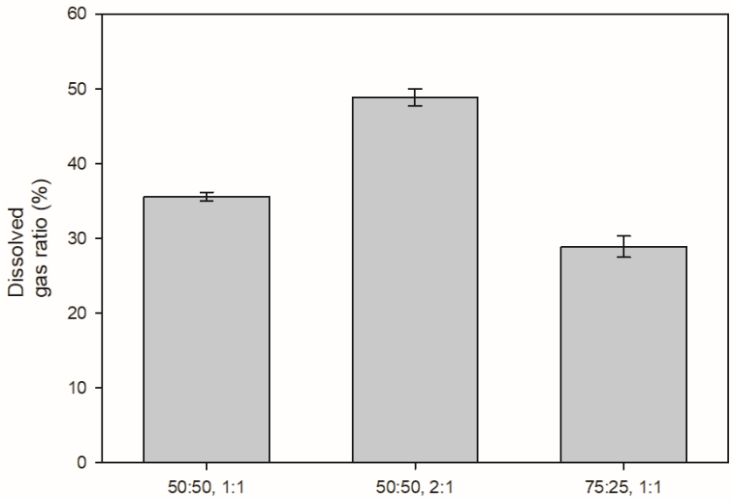


Fig. 38 Ratio of dissolved gas in 20 wt% NaI acetone solution

In the case of the 50:50 composition, the volume increase of the solution increased the proportion of dissolved gas as well as the tendency for the pure acetone experiment. The ratio of dissolved gas at 1: 1 volume ratio of solution to gas was lower at 75:25 than 50:50 condition. The reason is that the fraction of carbon dioxide initially supplied is low and the partial pressure is relatively low.

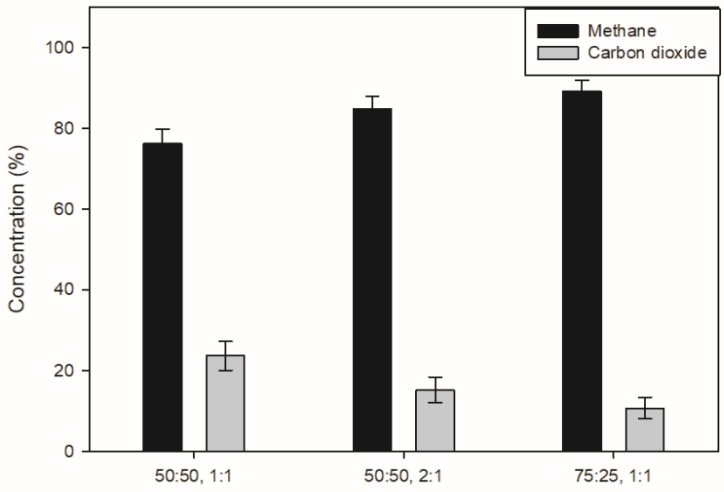


Fig. 39 Residual gas composition after reaction in 20 wt% NaI acetone solution

Fig. 39 shows the residual gas composition for an acetone experiment according to the volume ratio of solution to gas and the initial gas composition. The composition of residual gas after reaction in acetone solution with NaI concentration of 20 wt% was found to be increased when the amount of solution was increased as compared with that of pure acetone solution. Also, in the case of 1:1 with the same volume ratio, two conditions with different initial composition showed lower carbon dioxide ratio at 75:25. This is because the amount of gas contained in the initially supplied carbon dioxide was small. Therefore, when applied to the two-step process, the gas having the composition of the initial 50:50 has a composition of 75:25 and the treatment of the gas having the composition of 75:25 can treat the gas up to 90:10. Next, the composition of the degassed AD gas was confirmed in a 20 wt% acetone solution of NaI concentration.

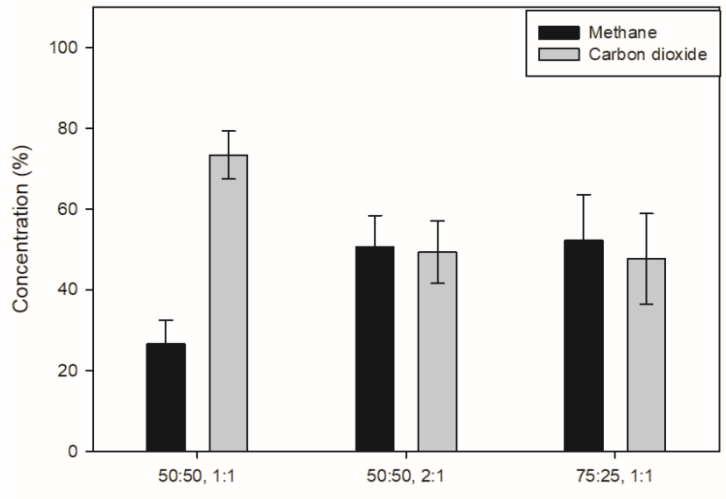


Fig. 40 Degassed AD gas composition after reaction in 20 wt% NaI acetone solution

When the gas having a composition of 50:50 was degassed after the reaction, the ratio of the degassed methane in the ratio of 2:1 when the volume of the solution was increased was high when the conditions of 1:1 and 2:1 were compared. Fig. 40 shows that the ratio of carbon dioxide in the residual gas composition after the reaction is relatively low. Compared with the initial composition of 50:50 and the initial composition of 75:25 at 1:1 volume ratio of solution to gas, the degassed high methane ratio was shown at 75:25. The reason for this is that the initial partial pressure of methane is high, resulting in the relatively more methane dissolution than the condition of 50:50. From these results, it was concluded that the condition of 1:1 volume ratio is better condition at 50:50 composition.

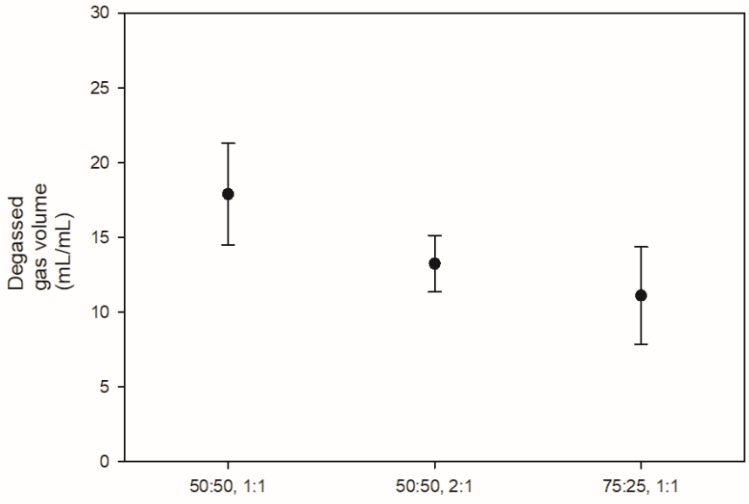


Fig. 41 Degassed AD gas volume after reaction in 20 wt% NaI acetone solution

Fig. 41 shows the volume of degassed AD gas for the acetone experiment according to the volume ratio of solution to gas and initial gas composition.

The volume of the degassed AD gas was observed to decrease as the volume ratio of the solution increased under the condition of the composition of 50:50. This tendency was consistent with water experiments. In addition, at a 1:1 volume ratio of the solution and the gas, the degassed volume was lower than that of 50:50 when the initial composition was 75:25, because the dissolved volume of the carbon dioxide was relatively small and the amount of degassed AD gas as well. From these experimental results, it was concluded that 1:1 condition of 50:50 gas is ideal in the same NaI concentration condition. However, the proportion of methane in the composition of the degassed AD gas was still high after addition of NaI salt. To overcome this disadvantage, the mixing of water with the advantage of degassing high carbon dioxide on the degassed AD gas side is considered. In the following experiment, the effect of addition of water was confirmed by comparing the binary system of pure acetone, NaI and acetone, the tertiary system of NaI and water, and acetone.

4.5.4 Effect of water addition in NaI/acetone solution

The experiment was carried out under the same conditions for a gas having a composition of 50:50 and a gas having a composition of 75:25 at Fig. 42. Experiments were conducted to confirm the effect of addition of water on the comparison of pure acetone, NaI / acetone binary system and NaI / water / acetone tertiary system. 20:0:80 indicates that the concentration of added NaI is 20 wt% and the concentration of acetone is 80 wt%. 20:20:60 indicates 20 wt% NaI, 20 wt% water, and 60 wt% acetone. At 50:50 and 75:25, the proportion of dissolved gas was reduced with acetone containing NaI. Compared with the binary system of NaI and acetone and the tertiary system with addition of water, it was slightly increased at 50:50 compared with the expectation that the dissolution rate would decrease with increasing water. The condition of 75:25 confirmed the decrease as expected. The composition of the residual gas was measured after the reaction.

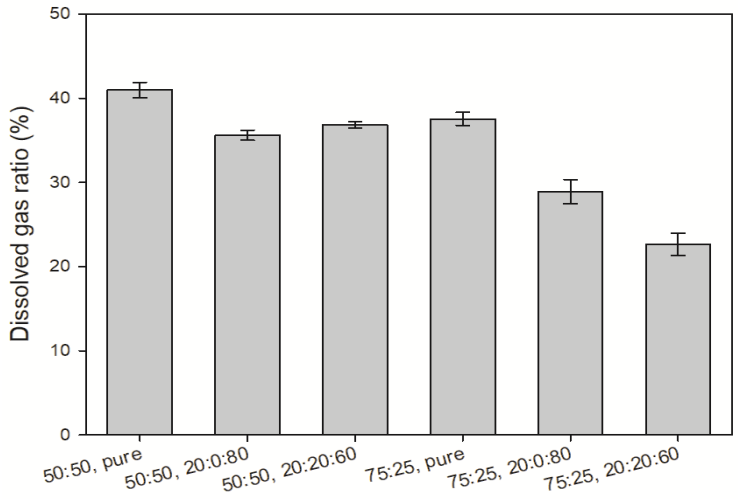


Fig. 42 Ratio of dissolved gas to pure acetone, NaI / acetone solution, NaI / water / acetone solution

The same trend was observed for the results for each experiment for the conditions of 50:50 and 75:25 at Fig. 43. In both cases, the ratio of methane in the residual gas decreased and the ratio of carbon dioxide increased in the case of pure acetone to the tertiary system to which NaI was added and NaI and water were added. This is because the amount of acetone, which plays a major role in the dissolution of carbon dioxide, is reduced. It was also confirmed that the gas condition of 75:25 showed a tendency to show a higher total carbon dioxide removal than the condition of 50:50. Likewise, the influence of the degassed AD gas was confirmed.

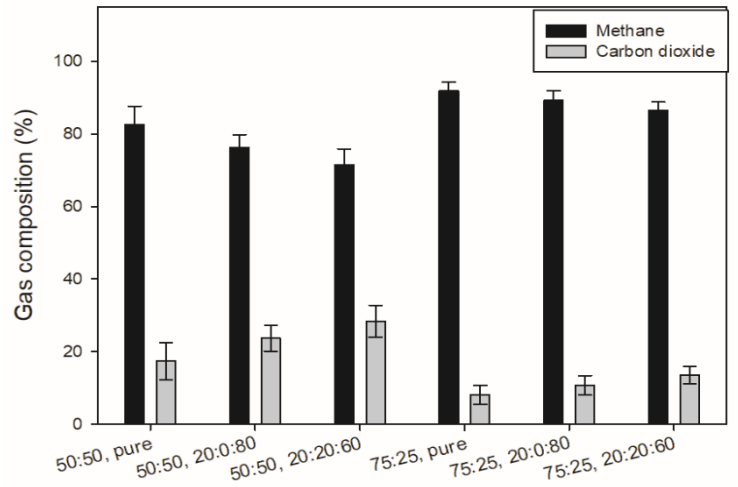


Fig. 43 Residual gas composition after reaction for pure acetone, NaI / acetone solution, NaI / water / acetone solution

Fig. 44 shows the composition of degassed AD gas for each case. When the composition of the degassed AD gas was observed, the tendency of the composition of the residual gas after the reaction was reversed. As NaI and water were added in the same gas condition, the ratio of degassed methane decreased and the ratio of carbon dioxide increased. Also, the overall ratio of degassed carbon dioxide in the gas composition of 50:50 was high compared to the ratio of 75:25. From these results, it is shown that the addition of NaI before, in addition to the addition of water, shows an improvement in the ratio of carbon dioxide in the degassed AD gas, which is an advantage of water. Finally, we observe the tendency for the volume of degassed AD gas.

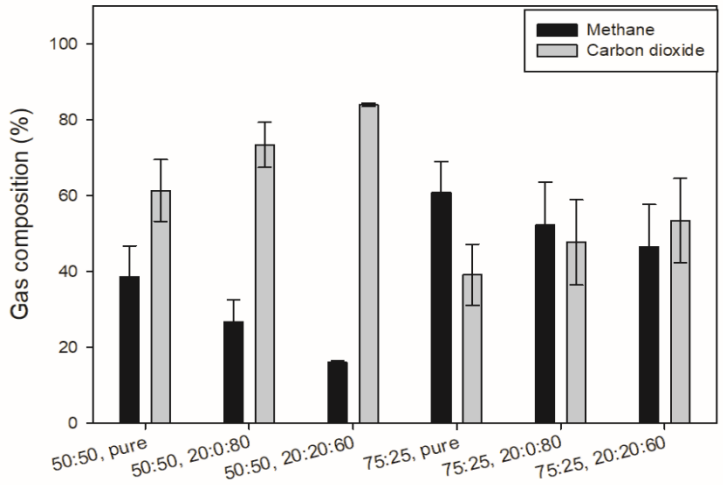


Fig. 44 Degassed AD gas composition for pure acetone, NaI / acetone solution, NaI / water / acetone solution

The results for the volume of degassed AD gas were compared for each experimental condition at Fig. 45. The results were also compared with those of pure acetone, NaI / acetone and NaI / water / acetone. The tendency was that the volume of degassed AD gas was reduced due to the addition of water as expected. However, in terms of the composition of the degassed AD gas, it can be confirmed that the addition of water can improve the gas composition. Based on these results, we conducted experiments to observe the experimental trends of water and acetone ratio in the tertiary system of NaI / water / acetone. The composition of NaI was fixed at 20 wt% and the ratio of NaI: water: Acetone was adjusted to 20:40:40, 20:20:60 and 20:10:70 by controlling the ratio of water to acetone.

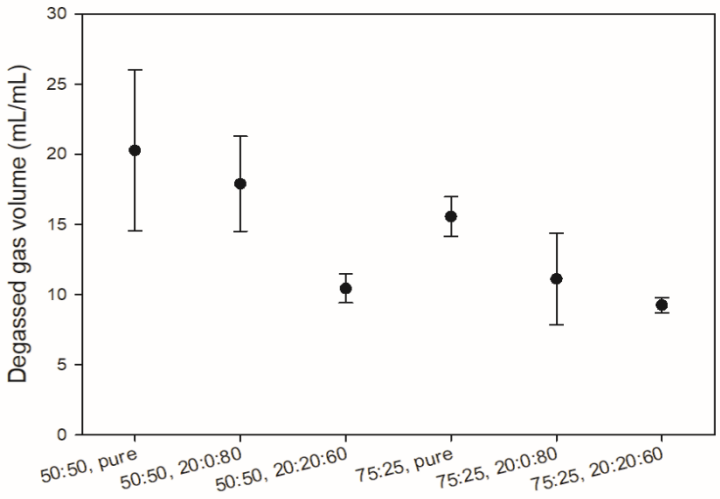


Fig. 45 Degassed AD gas volume for pure acetone, NaI / acetone solution, NaI / water / acetone solution

4.5.5 Effect of water/acetone ratio in tertiary system solution

Fig. 46 shows the ratio of dissolved gas to water / acetone ratio. In this experiment, a mixed gas of methane 50% / carbon dioxide 50% was used. The volume ratio of solution to gas was fixed at 1:1 and the amount of water and acetone was varied. Experiments were conducted on the case where the amount of water decreased and the amount of acetone increased from the left to the right. The tendency of the experiment showed that the proportion of dissolved gas increased as the amount of water decreased and the amount of acetone increased. This tendency confirmed that acetone plays a major role in dissolving the gas, and water was found to have a relatively low rate of dissolving the gas. However, in the case of 10 wt% of water and 70 wt% of acetone, it was confirmed that more than 40% of the initial feed gas was dissolved, but this amount did not show much difference with the dissolution rate in pure acetone under the same conditions. It was confirmed that the addition of a small amount of water does not significantly decrease the gas absorption rate of the solution.

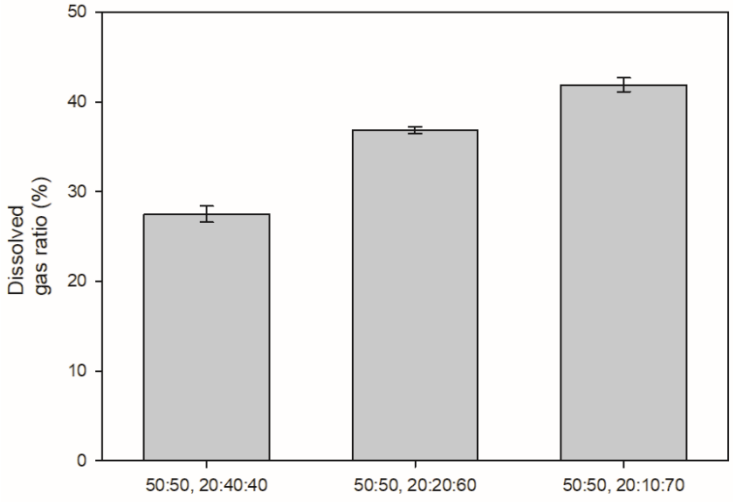


Fig. 46 Ratio of dissolved gas to water / acetone ratio in NaI / water / acetone tertiary system

The residual gas composition after the reaction was compared for the above experimental conditions at Fig. 47. As the amount of water increased, the residual ratio of carbon dioxide increased. Overall, the percentage of residual carbon dioxide in the tertiary system was higher than that of pure acetone. Under the same experimental conditions, the methane / carbon dioxide composition after the reaction of pure acetone was 82:18 and the composition of 74:26 when 10 wt% of water was added. Certainly, the addition of water showed a slight reduction in the dissolution rate of carbon dioxide. Next, the composition of the degassed AD gas was compared.

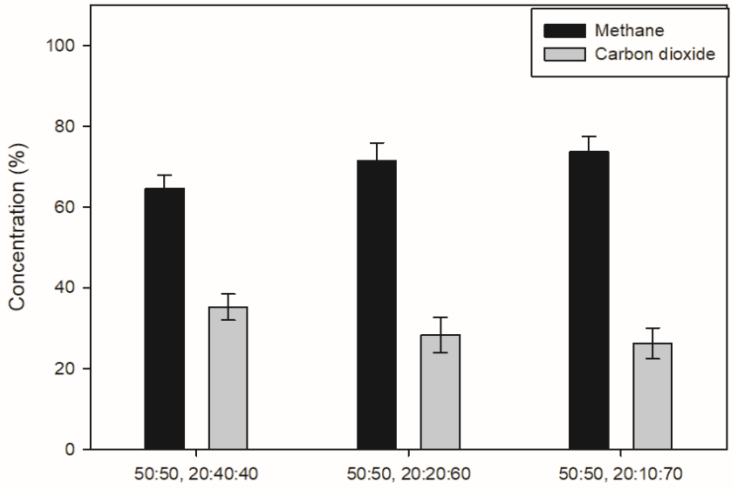


Fig. 47 Residual gas composition after reaction to water / acetone ratio in NaI / water / acetone tertiary system

The results of the tendency of the composition of the degassed AD gas to be opposite to the composition of the residual gas after the reaction were also observed at Fig. 48. As the amount of water increased, the proportion of degassed carbon dioxide increased. The composition of methane / carbon dioxide degassed in Pure acetone was 39:61. The proportion of methane in the degassed AD gas was high. However, when water is added, the proportion of degassed methane gradually decreases and the ratio of carbon dioxide increases. When 10 wt% of water is added, 23:77, when 20 wt% of water is added, 16:84, 40 wt% of water When added, it increased to 11:89. This result was confirmed to be similar to the composition of degassed AD gas, 7:93, under the same condition of pure water. Therefore, the addition of water for the dissolution and degasification of carbon dioxide was deemed to be useful in terms of the recycling of dissolved carbon dioxide. Finally, the volume of the degassed AD gas was measured.

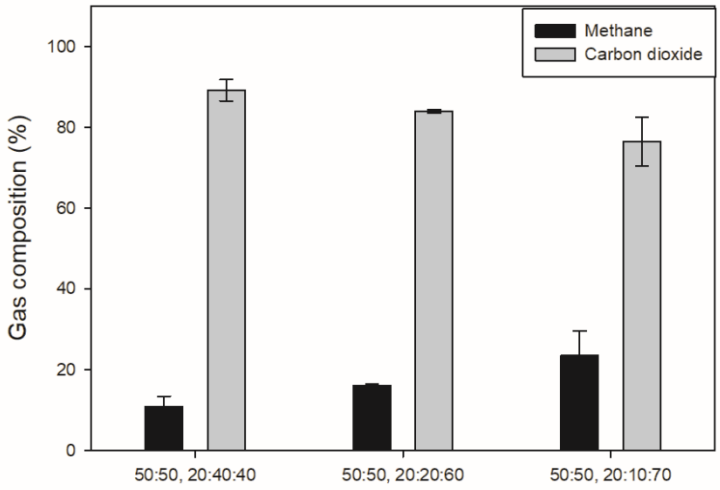


Fig. 48 Degassed AD gas composition to water / acetone Ratio in NaI / water / acetone tertiary System

In the experiment using water, the volume of degassed AD gas was relatively low in water compared to other solvents. As water was added, the results of this experiment showed a similar tendency at Fig. 49. The volume of degassed AD gas in Pure acetone was relatively higher than that of the solution containing water. As the water was added, the volume of the degassed AD gas gradually decreased, and when 40 wt% of water was contained, the value decreased about 4 times as compared with pure acetone. Considering all of the above four factors, the condition of NaI 20 wt% / water 10 wt% / acetone 70 wt%, which shows a good ratio of depleted carbon dioxide and volume, without decreasing the dissolution rate of carbon dioxide, the best results were obtained.

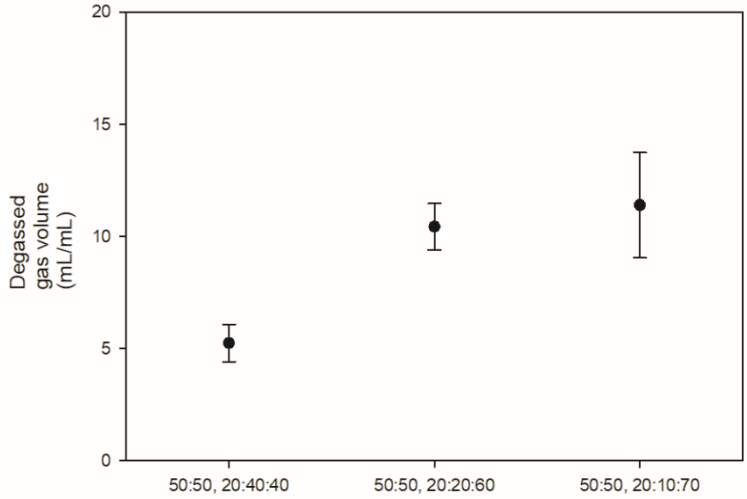


Fig. 49 Degassed AD gas volume to water / acetone ratio in NaI / water / acetone tertiary system

4.5.6 Results trend by simulation in tertiary system solution

Finally, we tried to observe the tendency of composition ratio of the three mixtures by using mixture design method. The ratio of water was 10 ~ 50%, the ratio of acetone was 40 ~ 80%, and the ratio of NaI was 10 ~ 30%. Experiments were carried out through nine experimental points that met the above range, and the tendency was calculated based on the results. The trends of residual carbon dioxide composition and degassed digestion carbon dioxide composition after the reaction were shown using Minitab 18 simulation.

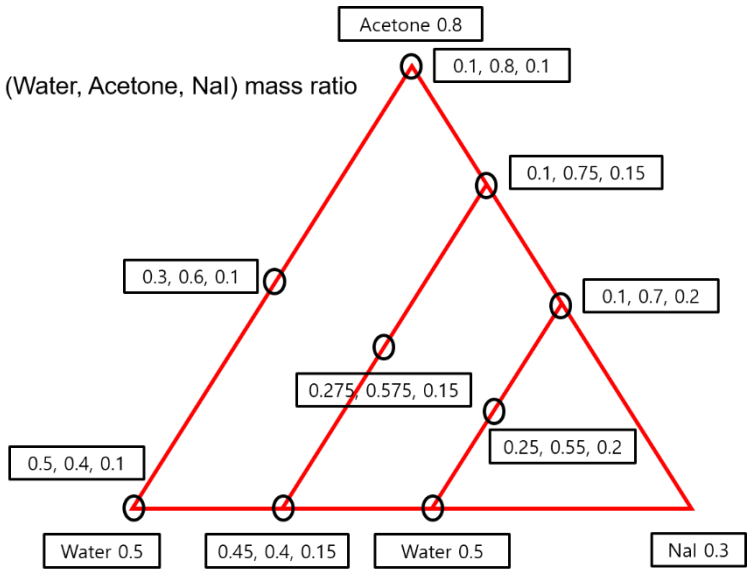


Fig. 50 The composition of each mixture used in the experiment

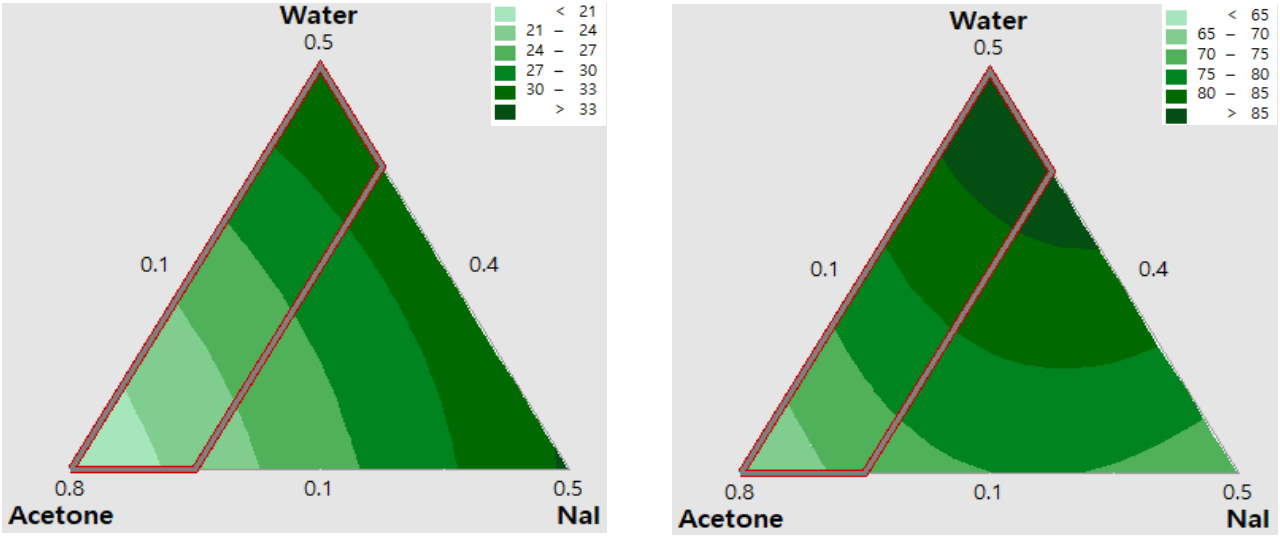


Fig. 51 (a) The tendency of residual carbon dioxide according to composition ratio of each component, (b) The tendency of degassed carbon dioxide composition according to composition ratio of each component.

In Fig. 51 (a), the composition of residual carbon dioxide showed a tendency to decrease when the amount of acetone was large and the amount of water and the amount of NaI were small. This tendency is consistent with the experimental results that acetone plays a crucial role in the dissolution of carbon dioxide. In addition, when water and NaI were added as additives, the amount of dissolved carbon dioxide decreased and the composition of residual carbon dioxide tended to increase slightly. Fig. 51 (b) shows the tendency of the composition of degassed carbon dioxide by simulating the same method. In contrast to Fig. 51 (a), the composition of degassed carbon dioxide tended to increase when the amount of water and NaI was large, and the composition of carbon dioxide tended to decrease with increasing amount of acetone. From the above two simulations, it was found that the composition of residual carbon dioxide and the composition of degassed carbon dioxide were almost inversely proportional to each other, and it was concluded that the optimum conditions for each condition could be found to be advantageous for the continuous process.

5. Conclusions

This study was conducted on the solvents that can be used in the absorption process to separate carbon dioxide and methane from biogas. In this study, to overcome the disadvantages of amine solvent, which is widely used in the absorption process, in the regeneration process, we observed a solvent that can absorb carbon dioxide through physical absorption and easily regenerate the solvent. From the reference, it was confirmed that the substance having carbonyl group or ether bond can increase the solubility of carbon dioxide. Experiments on various functional groups were carried out in addition to this functional group. In terms of the solubility of carbon dioxide, it was confirmed that each of the solvents had high solubility in carbon dioxide, but solubility in methane was also high. There was no selectivity for the reference because of the solubility test for pure carbon dioxide. Experiments on artificial seawater conditions have confirmed that the addition of salt increases the carbon dioxide ratio in the degassed AD gas without significantly reducing the carbon dioxide solubility in the solution. For the pure solvent test, acetone in various solvents was considered to be suitable for the purpose of the experiment. Through the mixed solution for acetone, we tried to solve the problem of having a high methane ratio in the composition of degassed AD gas which is a disadvantage of acetone. It was confirmed that the carbon dioxide ratio of the degassed AD gas was improved by adding NaI which is high in solubility to acetone, and it was confirmed that the carbon dioxide ratio of the degassed AD gas, which is an advantage of water, can be increased in the tertiary system added to water. It has been concluded that the proper mixing of water and salt in the solvent can show improved results in terms of degassed AD gas while maintaining some of the carbon dioxide solubility of the solution. Further research is needed to study other solvents, such as acetone, which are capable of physical absorption and are capable of removing carbon dioxide. In addition, it is necessary to study the application of NaI, which can play a role in helping to degas the dissolved gas.

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